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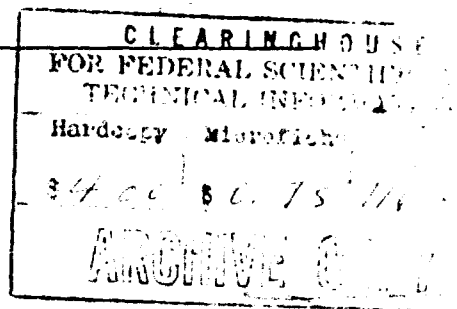
Thesis Title WATER RECOVERY FROM HUMAN LIQUID WASTES

BY DISTILLATION AND CHEMICAL OXIDATION

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WASHINGTON UNIVERSITY
SEVER INSTITUTE OF TECHNOLOGY

WATER RECOVERY FROM HUMAN LIQUID WASTES
BY DISTILLATION AND CHEMICAL OXIDATION

BY

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Prepared under the direction of Professor Edward Edgerley, Jr.

A thesis presented to the Sever Institute of
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ABSTRACT

WATER RECOVERY FROM HUMAN LIQUID WASTES
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The recovery of potable water from human urine by atmospheric and vacuum distillation and by chemical oxidation was investigated utilizing the parameters of organic carbon, BOD, and COD.

Linear relationships existed between organic carbon, BOD, and COD for the human urine samples studied. These relationships were as follows: organic carbon to BOD ratio equals 1.34, BOD to COD ratio equals 0.52, and organic carbon to COD ratio equals 0.64.

The vacuum distillation of urine yielded a water suitable for human consumption.

The chemical oxidation of human urine by ozonation was not found to be a practical means of treatment and water recovery due to the excessive quantities of ozone required.

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WATER RECOVERY FROM HUMAN LIQUID WASTES BY DISTILLATION AND CHEMICAL OXIDATION

1. INTRODUCTION

With the increasing population and increasing per capita water demands, certain areas will soon face the problem of needing more water than can be obtained from local water supplies. This projected water deficit has instigated an interest in water reuse, using treated waste waters as a public water supply source.

The idea of water reuse has also been proposed by researchers in the study of systems which operate in environments foreign to man, such as space vehicles. Here the problem of water supply is even more pronounced as the system is isolated from the external and all water must be obtained from within the vehicle.

1.1 THE IMPORTANCE AND NECESSITY OF WATER RECOVERY FOR REUSE

In 1960, the United States used an estimated 322.9 billion gallons of water per day (1). Of this, 22.0 and 135.0 billion gallons per day was used for public water supplies and irrigation, respectively. The forecasted water use for

1975 is 449.7 billion gallons per day with 29.8 billion gallons per day for public water supplies and 169.7 billion gallons per day for irrigation (1). This large increase over this 15 year period will cause large urban centers and areas in southwestern portion of the United States to face water shortage problems as the available sources of water will not appreciably increase during this period.

On a smaller scale, closed space systems are running into water logistics problems as missions become days and months rather than hours. All water for drinking and hygienic purposes must be obtained from within the vehicle once the mission starts. This can be accomplished by carrying an initial water supply for the duration of the mission or by recovering water from wastes during the mission. The former means of water supply requires more power during the take-off as the stored water adds to the weight of the system. This leaves the latter as the logical solution to the problem.

1.1.1 Domestic Recovery and Reuse

Pure water makes up 99.9 percent by weight of sewage (2). The use of a ton of water to carry away a few pounds of waste constitutes a luxury that some communities can no longer afford. Therefore, water recovery for reuse must be implemented.

Some have questioned whether the public would accept a "secondhand" water, for aesthetic reasons, even if it was

clear and palatable (2). Today, in many cities of the United States located on rivers, something not far from direct reuse is the general rule. In many instances, large quantities of organics discharged into a river upstream prevent the natural degradation process to occur and thus diluted sewage is used as the public water supply by downstream cities. Examples of the above are the cities located on lower reaches of the Mississippi and Missouri Rivers.

At first glance, the solution to the problem of domestic water reuse would be to connect the effluent line from a conventional sewage treatment plant to the influent line of a conventional water treatment plant as was essentially done at Chanute Kansas during drought flows on the Neosho River (3). There are, however, certain refractory and inorganic contaminants in sewage which are not removed by present water and waste-water treatment processes. With each reuse, these contaminants would be increased by an additional increment. After a short while, such contaminants as detergents (alkyl benzene sulfonates), DDT, orthonitrochlorobenzene, pyridine, diphenyl ether, kerosene, nitriles, and a variety of substituted benzenes would start appearing in the consumer's glass of water (4). Inorganics, such as chlorides, nitrates, carbonates, and sulfates, would also reach high concentration levels in the water supply. Eventually, these contaminants would build up to a concentration level where they might have physiological effects as well as aesthetic complaints.

Therefore, effluents from secondary waste treatment plants must be given a "tertiary" treatment if the problems mentioned above are to be avoided. Several different "tertiary" treatment processes have been proposed to make water ready for reuse (5) (6).

Some communities use treatment plant effluents to recharge low ground water basins that feed nearby wells (7). It is also channeled to serve as irrigation water by some cities (7). These practices are indirect water reuse.

1.1.2 Industrial Water Supply

Industry now uses nearly one-half of the 322.9 billion gallons of water produced for public and private use, or 150 billion gallons daily. By 1975, the industrial demands have been variously estimated from 250 to 400 billion gallons per day or approximately two-thirds of the water produced (8). Approximately one-half of the water used by industry is required for process cooling water and boiler feed purposes. Only two percent of all of the water used by industry is actually consumed, with the remainder returned to a receiving source (8).

Economic interests dictate that process industries choose water of the lowest total cost. So, in water short areas, more than thirty industrial plants in the United States have chosen municipal waste water as a major or supplementary supply (9). This saves clean water for domestic use.

1.1.3 Water Recovery and Reuse in Closed Environments

As space missions increase in duration, the logistics for a crew to survive will increase the payload weight and thus limit future voyages. Typical logistic values are as follows (10):

Logistic Requirements	Weight (lbs/man/day)
Water (for drinking and preparing food only)	4.9
Food (dry basis, 95% digestable)	1.1
Oxygen	2.4

The above values show that water is the heaviest logistic requirement. Since all the water must come from within the vehicle, a water recycling system must be utilized.

Various means of water recovery in closed systems have been proposed. These include the conventional waste treatment means such as activated sludge and trickling filters but these biological systems require too large an initial weight to be feasible for missions other than of a permanent nature, such as moon stations or permanent orbiting satellites (11). The treatment methods for recovery of water from liquid wastes (urine and wash waters) include distillation, chemical oxidation, electrodialysis, ultrafiltration, osmosis, solvent extraction, and various freezing methods. All of the above require much more research before a practical application can be made.

1.2 COMMON PROBLEMS OF REUSE

The recovery of water from domestic sewage and closed system wastes, may at first glance, seem far apart and unrelated. The domestic wastes consists of human feces and urine diluted by large quantities of storm runoff and domestic wash waters, while the closed system waste consists of human feces and urine diluted by small quantities of body wash waters. But both recovery processes have one thing in common; that being, to recover drinking water from a wastewater source. Any work done in one of these areas may find application in the other area. This is particularly true of work done in closed system wastes, as domestic wastes from a household, which are more concentrated than municipal sewage, may eventually have to be treated at and reused in the individual home in water short areas (12).

2. PURPOSE AND SCOPE

Presently, much work is being done by researchers concerned with water recycling in closed environments. Most of these studies are concerned with human urine and wash waters and use parameters such as ammonia nitrogen, color on the cobalt scale, turbidity on the silicon dioxide scale, chlorides, conductivity, and odor to measure the acceptability of the recovered product from various recovery processes. Very little, if any, work has been done utilizing the parameters of the Environmental and Sanitary Engineer; namely, BOD (biochemical oxygen demand), COD (chemical oxygen demand), and organic carbon. These parameters have been used successfully in both biological and chemical treatment systems on earth to give an indication of organic content and its nature before, during, and after treatment. These valuable tools should be incorporated in any research dealing with wastewater reuse.

Therefore, the purpose of this thesis was to add to the basic knowledge of water recovery systems utilizing the parameters commonly employed in Environmental and Sanitary Engineering.

This study was accomplished by recovering water from human urine by the distillation process, both atmospheric and vacuum, and by chemical oxidation with ozone. The vacuum distillate product was also ozonated in an attempt to get more effective treatment. The processes were monitored by

all the parameters used by researchers in water recycling and by the major parameters of the Environmental and Sanitary Engineer. Infrared analyses also monitored all the treatment processes in an attempt to determine the why and how of the recovery process.

In addition to and in conjunction with the above studies, a synthetic human waste was developed from a review of the literature of the make-up of human urine. This synthetic urine was recycled for comparison with the human wastes. A synthetic waste would be of use to research in this area as it would give a constant base for comparison studies of different recovery processes.

3. LITERATURE SURVEY

The purpose of this literature survey was threefold. First, current and forecasted practices for reuse of domestic waste-waters were reviewed in order to determine a base from which to study the closed system results and for cross comparison reasons. Secondly, if work was to be done with recovering water from human waste, the composition of the waste and the criteria for the acceptability of the recycled product must be defined. Finally, the techniques and characteristics of work done by other researchers in the area of water recovery systems was surveyed.

3.1 PRESENT DOMESTIC WASTE-WATER REUSE PRACTICES

As was shown in Sections 1.1 and 1.1.1 of this study, some communities can no longer afford to use a ton of water to carry away a few pounds of waste and thus, they are now being forced to consider water recovery for reuse. The conventional secondary sewage treatment process will not remove all of the contaminants and hence the effluent cannot be treated by a conventional water treatment plant without a "tertiary" treatment process.

Concentrated work in the area of waste-water treatment for intentional domestic reuse began when, in 1960, the United States Public Health Service initiated an Advanced Waste Treatment Research Program. The scope of this program's work was to study means of alleviating the nation's growing water pollution problems and to develop methods of

renovating waste-water for direct and deliberate reuse (13). Research activities of the program have shown the possible processes for advanced waste treatment to include adsorption, electrodialysis, emulsion separation, évaporation, extraction, foaming, freezing, hydration, ion exchange, and chemical or electrochemical oxidation. Researchers, in this area, have taken these initial concepts and made practical applications to the domestic reuse problem.

One such application was by Keefer (6) who has proposed using rapid sand filtration, oxidation ponds, microstrainers, chemical precipitation, or further biological treatment for waste treatment plant effluents to obtain a product for reuse. A somewhat simpler and more explicit process was described by Culp (5). Culp's system uses pH adjustment and coagulation followed by sand filtration and then followed by activated carbon columns. This system is reported to have removed the ABS and phosphate fractions of synthetic detergents and complex organic contaminants not affected by conventional biological treatment (5).

All work done in this area has not been done by orthodox water and waste-water treatment processes. Karassik and Sebald (14) have proposed the use of their patented "pasteurizer" process on treatment plant effluents. The process consists of running the effluent through an activated carbon pressure filter and then through a three stage

series of pasteurizers and sterilizer heated from 60 to 298 degrees Fahrenheit. The water is then passed through an aerator before it is returned to the public.

The simplest and yet most expensive process of water recovery is the distillation process. In an article by Hickman (15), the various types of distillation for large scale domestic applications are reviewed. Hickman says that distillation has uses in the water reuse area: First, it can be used to treat water that has been treated by other processes, and in which an impurity remains that can only be removed by distillation. Second, it can give complete treatment to smaller communities where a diversity of treatment processes for recycling is not warranted or available. Third, it can find use in disaster conditions-flood, epidemic, or contamination due to radioactive fallout- when nothing but a complete change-of-phase treatment can be trusted. And fourth, distillation is an effective means of drying sewage concentrates.

General work on recovery of water by chemical oxidation has been done by Gaudy (16) and recovery by solvent extraction by Zeitoun (16). The results of these processes appear to indicate their applicability to small volume reuse.

An indirect water reuse, which results in increased water supplies, is the recharging of low ground water basins to feed nearby wells with treatment plant effluents. Many

communities practice this procedure and the method is presently suggested by many authorities for use by other water short municipalities (7)(17)(18)(19).

The direct use of domestic sewage or the use of partially treated sewage as a source of industrial process water is practiced by many industries (7)(8)(9)(19)(20)(21)(22). This amounts to large savings in water as it is estimated that industry will require two-thirds of the total water produced in years to come and process waters account for 98 percent of the industrial requirements (8).

3.2 HUMAN WASTES

In order to design and operate a water recovery system, the source material must be characterized as to origin and nature.

3.2.1 Composition of Human Wastes

Human wastes in closed systems fall into three general classes; urine, feces, and insensible water from respiration and perspiration. A man's water balance and composition of the above wastes varies considerably, depending upon a number of factors such as body weight, level of activity, temperature of environment, and diet. The following values for the water balance are the accepted values for the average man per day (10)(23):

Intake(grams/day/man)		Output(grams/day/man)	
Drinking Water	1200	Water in Urine	1400
Water in Food	1000	Water in Feces	100
Water of Oxidation	<u>300</u>	Insensible Water (respiration and perspiration)	<u>1000</u>
Total	2500	Total	2500

All human wastes contain an appreciable amount of water. Urine contains 90 to 95 percent, feces 75 percent, and respiration and perspiration contain approximately 99 percent water.

3.2.2 Sources of Water for Recovery Systems

The lower water content of feces, relative to the other human wastes, and the odor and bacterial level of feces, have all but excluded its incorporation in water recovery work except for closed ecological systems (10)(11)(23). Ingram (11) states that feces should be deposited in plastic bags and stored until the return flight to earth.

The insensible water, from respiration and perspiration, does not contain the variety of contaminants and concentration levels encountered in urine. It also varies more in composition and amount than human urine due to the body function of water and temperature balance with the environmental conditions. Since the waste is so uncertain in composition and only serves to dilute the more concentrated urine, water recovery systems often will recover water from the stronger urine waste (10)(24).

The composition of human urine is very complex. Total solids amount to almost five percent by weight, about half of which is urea. Table 1 represents the major components of average normal urine (23). Urine, as normally excreted by a healthy individual, does not contain any pathogenic organisms (10). The odor of fresh urine is moderately unpleasant, while that of stale urine is strongly disagreeable.

3.3 QUALITY REQUIREMENTS FOR REUSED WATER

In recent government contracts for water recovery systems, contract specifications call for recovered water to meet United States Public Health Drinking Water Standards (10)(23). These specifications for recovered water, with emergency condition standards, are shown in Table 2 (10).

McKee (25) takes objection to these standards since they are standards of excellence, not criteria of human health or limits for the maintenance of a healthful condition in space. McKee says that these standards are extremely conservative as they are designed to protect children from fluorides and nitrate, to protect aquatic life and gold fish in aquaria with respect to chromates and copper, and to meet the threshold limits of taste in the case of copper, iron, zinc, and manganese. In his opinion, these standards should definitely not be applied blindly to the determination of water quality to be met by reclamation systems in space. In many instances, short-term exposure to concentrations considerably in excess of the Public Health Service standards would produce no measurable detrimental effect.

TABLE 1
CHEMICAL COMPOSITION OF URINE (23)

Constituent	Daily Excretion Amount (grams)	% Solids By Weight
Water	1200	
Solids	60	4.76
Urea	30	2.38
Hippuric Acid	0.7	0.0555
Uric Acid	0.7	0.0555
Creatinine	1.2	0.0954
Indican(Iodoxy) Potassium Sulfate)	0.01	
Oxalic Acid	0.02	
Allantoin	0.04	
Amino Acid Nitrogen	0.2	
Purine Basis	0.01	
Phenols	0.2	
Cl as NaCl	12.0	0.954
Na	4.0	
K	2.0	0.159
Ca	0.2	
Mg	0.15	
Sulfur, total as S	1.0	
Inorganic Sulfate as S	0.8	0.0635
Neutral Sulfur as S	0.12	
Conjugated Sulfates as S	0.08	
Phosphate as P	1.1	0.0875
Ammonia	0.7	

TABLE 2
SPECIFICATIONS FOR RECOVERED WATER (10)

1. Bacteriological Quality:

The bacteriological tests consists primarily of examining standard portions for organisms of the coliform group. Not more than 10% of the portions examined may show the presence of such organisms.

2. Physical and Chemical Characteristics:

The following maximum limits apply.

Turbidity	-- 10 ppm (silica scale)	Copper	-- 3.0 ppm
Color	-- 20 ppm (cobalt scale)	Iron and Manganese*	-- 0.3 ppm
Taste	-- Not objectionable	Magnesium	-- 125 ppm
Odor	-- Not objectionable	Zinc	-- 15.0 ppm
Lead	-- 0.1 ppm	Chloride	-- 250 ppm
Fluoride	-- 1.5 ppm	Sulphates	-- 250 ppm as SO ₄
Arsenic	-- 0.05 ppm	Phenolic	-- 0.001 ppm as phenol
Hexavalent chromium	-- 0.05 ppm	Total Solids	-- 500 ppm

3. Emergency Conditions:

Under emergency conditions the following limits apply:

Total Solids	-- 2000 ppm	Magnesium	-- 500 ppm
Chlorides	-- 1000 ppm	Magnesium Sulphate	-- 1000 ppm
Sulphates	-- 750 ppm		

*Original reference lists iron and magnesium.

McKee's opinion on water standards was substantiated by Sendroy and Collison (24). These researchers ran toxicity tests of the water recovered from human urine on young male rats. Even in their worst product, which had an ammonia content of 50 milligrams per liter and a high organic content, the recovered water was wholly innocuous to the rats and upon conclusion of the experiment after 30 days, a gross autopsy yielded negative results in all the vital organs.

From the literature, it would appear that there are varied opinions on recovered water standards but the consensus is that standards should be set as high as the Public Health Service standards until more work can be done with recovered water and its effect on humans.

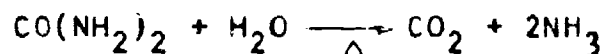
3.4 TREATMENT AND RECOVERY METHODS FOR HUMAN LIQUID WASTES

The various treatment and recovery processes presently being studied by other researchers in the area of water recovery are reviewed in this section.

3.4.1 Atmospheric Distillation

Simple atmospheric distillation is the simplest and best understood of the recovery processes. Slower moving ions are retained in the original boiling liquid while the freer moving substances go into the vapor state and are condensed and collected. The atmospheric distillation of

urine produces a product having an ammonia odor and a high pH (26). The ammonia originates from urea, which, being an amide, is hydrolyzed by boiling with water. The reaction is as follows:



Sendroy and Collison (24) acidified the urine before the distillation and much of the ammonia was retained with a consequent reduction in the amount carried over into the distillate. However, the distillate contained chloride from the HCl produced by the reaction of the chloride salts with sulfuric acid. The acid treatment also caused hydrolysis and liberation of other volatile products, among them the odoriferous compound urinod.

In all cases of atmospheric distillation, the recovered product still requires further treatment with activated carbon and ion exchange resins (23)(24)(26).

3.4.2 Vacuum Distillation

Vacuum distillation lowers the distillation temperature by reducing the atmospheric pressure above the urine. A vacuum distillation system with a boiling temperature below 98 degrees Fahrenheit does not decompose urea and hence, the distillate does not contain ammonia. A large volume of work has been done in the area of applying the vacuum distillation process to water recovery from human urine (10)(11)(23)(26)(27).

There are, however, many volatile organics in urine that will go into the vapor state at temperatures below 98 degrees Fahrenheit. David (28) has developed a system to overcome these problems. This system is vacuum distillation at 90 degrees Fahrenheit and a vacuum of 1.16 pounds per square inch with one major modification. The vapor is oxidized in the presence of a catalyst and high temperatures. The catalyst is platinum gauze and does not seem to be effected by the reaction and the temperature is 960 degrees Fahrenheit. The vapor is then condensed and ready for use.

3.4.3 Freeze Crystallization

When urine is partially frozen and the ice formed is washed free of the mother liquor and melted, fresh water should be obtained. The ice formed, however, always consists of a mass of minute crystals that retain a comparatively great volume of the original urine which is not easily separated by ordinary draining, filtering, centrifuging, or washing (23)(26).

3.4.4 Chemical Treatment

The amount of work done with chemical treatment of human urine is not as extensive as some of the other processes. The major chemical processes for the removal of urea is by the enzyme urease (29)(30). The reaction is as follows:



Brown (30) followed this urease-reacted urine with strong chemical oxidating agents, sodium and calcium hypochlorites. The results were not impressive because of the high concentrations of oxidizing agents required to get only a partially treated waste.

3.4.5 Electrodialysis

The membrane electrodialysis process uses synthetic ion-exchange membranes. These membranes are thin sheets of cation- or anion-exchange resins and are therefore selective as to the migration of cations or anions, respectively. They exhibit high electrical conductivity and low permeability to the passage of water. Upon the application of an electromotive force, the positive ions pass through the cation-permeable membrane, whereas the negative ions move in the opposite direction and pass the anion membrane. Thus the water passing between alternate membrane pairs is depleted of salt, whereas that passing through the intervening pairs is enriched. Electrodialysis, however, will remove only ions and not urea. For this reason, urine has to be treated first with an enzyme converting all the urea to ammonia and carbon dioxide, which will form ionic ammonium carbonate with pH adjustment, which then can be removed by electrodialysis (26).

3.4.6 Solvent Extraction

The solvent extraction process is a liquid-liquid extraction process in which a solvent extracts the water

from the wastes. The organic solvent, such as tertiary octylamine (10), dissolves more water at low temperatures than at high temperatures. As the temperature of the extract is raised, the water separates from the solvent. The water must then be treated further with activated carbon to make it potable and to remove the solvent for recycling. Hendel (26) does not favor the solvent extraction process for space flights because of the required heavy, bulky equipment and also the probability of contaminating the cabin air with organic solvents.

3.4.7 Adsorption Filtration and Ion Exchange

The adsorption filtration and ion exchange process consists of an adsorbent to remove color, odor, and organic contaminants and ion exchange media to remove the positive and negative ions from human urine. Both processes would be a column system. The most common adsorbents used are activated carbon, silica gel, fullers earth, kieselguhr, and inorganic oxides. The ion exchange resins that could be readily adapted for treating urine are the high capacity silver and barium zeolites (23). The weight required for a single recovery cycle is too high and the system would only be practical for long duration mission since the ion exchange media can be regenerated, thus reducing the ratio of weight of purifying material to weight of water recovered.

3.5 SUMMARY

The above literature survey has covered the major work done by researchers in the area of water recovery for reuse. In order to make a concrete application of this review to this present study, the purpose of which was stated in Section 2, a summary of the findings would be appropriate here.

The most promising types of water recovery systems for use in closed space systems are the atmospheric and the vacuum distillation processes. The majority of the water reclamation studies on human wastes have been done with these systems and the results appear to indicate that they are most efficient and reliable. The atmospheric distillation process has less equipment and initial weight than the vacuum distillation process but the latter method yields a distillate that contains far less ammonia carry-over.

Chemical treatment methods for water reuse have not been studied as extensively as some of the other treatment methods. Some work has been done with enzyme reactions but particularly lacking, is work done with direct chemical oxidation of human urine with a strong oxidant such as ozone.

In all work in water reuse, researchers use the more physical parameters such as ammonia nitrogen, color, turbidity, chlorides, conductivity, and odor to measure the acceptability of the recovered product. Little work has been done utilizing the parameters commonly used by the Environmental and Sanitary Engineer; namely, BOD, COD, and organic carbon. Ingram (11)

did use BOD and COD as parameters when he studied the activated sludge and trickling filter processes as treatment methods, which he ruled out because of low efficiencies and excessive weight requirements. But when, in the same paper, Ingram analyzed the vacuum distillation process, he conformed with other researchers in this area and used the more physical parameters as mentioned earlier. These valuable organic parameters have been excluded from research in this area.

4. MODE OF STUDY

In order to accomplish the purpose of this thesis, which was to add to the basic knowledge of water recovery systems utilizing the parameters of Environmental and Sanitary Engineering, a research study was undertaken in which the recovery of water from human and a synthetic urine was accomplished by distillation and chemical oxidation with both processes being monitored by all the parameters used by researchers in water recycling and by the major parameters of the Environmental and Sanitary Engineer.

4.1 SELECTION OF PARAMETERS

The parameters of BOD (biochemical oxygen demand), COD (chemical oxygen demand), and organic carbon, being the parameters most commonly employed in Environmental and Sanitary Engineering, were the primary monitors of the recovery processes. These parameters were used in the recycling systems to give an indication of organic content and its nature before, during, and after treatment.

In an attempt to correlate this study with other research in this area, the parameters commonly employed by different investigators were also used to check the distillation and chemical oxidation processes (10)(11)(23)(24)(27)(29). The parameters used are as follows: ammonia nitrogen, pH, threshold odor, color, chlorides, specific resistance, total solids, and turbidity.

A parameter which had not been utilized previously was infrared spectrophotometric analysis. This tool was incorporated into the present study to monitor all the recovery processes in an attempt to determine the why and how of these processes.

4.2 URINE SAMPLES

4.2.1 Human Urine

Human urine samples were obtained from the staff and graduate students of the Department of Environmental and Sanitary Engineering, Washington University, St. Louis, Missouri. Composite samples were used as the starting raw waste for the treatment processes. Individual samples were also collected and analyzed raw to get a range of values for human urine with the parameters used in this study.

4.2.2 Synthetic Urine

In an attempt to obtain a constant reproducible urine waste for comparison studies of different recovery processes, a synthetic human urine was developed. This synthetic was made from a composite of the concentrations of the major constituents in human urine which were found in the literature. The synthetic then had the same recovery processes performed on it as were performed on human urine, using the same parameters, so that the former could be compared with the latter.

4.3 DISTILLATION OF SYNTHETIC AND HUMAN URINE

4.3.1 Atmospheric Distillation

The recovery of water from human and synthetic urine by atmospheric distillation was accomplished by boiling the initial waste at a temperature slightly above 100 degrees Centigrade until vapors were evolved. These vapors were then passed through a condenser where the liquid condensed was collected as the recovered product.

4.3.2 Vacuum Distillation

The recovery of water from human and synthetic urine by vacuum distillation was accomplished by essentially the same process as atmospheric distillation with the exception that the boiling temperature was only 36 degrees Centigrade due to the reduction of the pressure above the urine to 1.5 inches of mercury by the application of a vacuum.

4.4 CHEMICAL OXIDATION

4.4.1 Selection of Ozone as Chemical Oxidant

If a chemical oxidation process is to be applicable to closed system water reuse, the oxidant must be a strong agent and easy to carry or generate. Ozone is a very strong oxidizing agent with an oxidation potential of -2.07 volts as referred to the hydrogen potential at 25 degrees Centigrade and it is second only to fluorine in oxidizing strength (31)(32). Ozone is reported to react rapidly with typical groupings that can be encountered

in human urine, namely, such groups as $-SH$, $=S$, $-NH_2$, $=NH$, $-OH$, and $-OH_2$ (31). Also, ozone is simply produced by an electrical discharge through dry air or dry oxygen (32). Thus the strength and low weight requirements of ozone make it the logical oxidant to be used.

4.4.2 General Process

The chemical oxidation of urine was accomplished by bubbling ozone, from a ozonator with a calibrated ozone concentration per flow unit and time unit, through the urine sample. The ozone content of the gas after it has been bubbled through the sample is measured and the difference between this value and the production value for a given time is the quantity of ozone absorbed by the sample. The rates of ozone uptake with time were determined during the process in an attempt to find the most economical ozonation time and in an attempt to determine the steps in the oxidation process.

Raw human urine and raw synthetic urine were subjected to chemical oxidation and the vacuum distillates of human and synthetic urine were also ozonated in an effort to obtain a more effective treatment.

5. EXPERIMENTAL METHODS AND PROCEDURES

5.1 SAMPLE PREPARATION

5.1.1 Human Urine

As mentioned earlier, human urine samples, to be used for the recovery processes, were obtained from the staff and graduate students of the Department of Environmental and Sanitary Engineering, Washington University, St. Louis, Missouri. On the days prior to the recovery operations, six one-gallon bottles were placed in strategic areas of the department for use by the staff and students. The contents of these bottles were combined into a overnight storage bottle at the end of the day. The composite sample, which represented approximately twenty persons, was then preserved until the next morning by a layer of toulene. This layer of toulene prevented bacterial degradation of the urine and permitted storage at room temperatures to eliminate coagulation of proteins which occurs at cold storage temperatures (33). On the following day, the human urine was siphoned from the overnight storage container to a intermediate container for future transfer to the type of recovery system being studied that day.

In addition to the composite samples, individual samples were collected to obtain a range of values for human urine using the parameters of this study. On the

mornings of runs. these individual samples were collected at home by graduate students and brought into the laboratory for analysis. No preservation was needed for these samples.

5.1.2 Synthetic Urine

The development of a synthetic urine, to be used as a constant base for comparison studies of recovery techniques, was the result of a compilation of the major constituents and their concentrations as normally found in human urine as reported in the literature. Spector (34) gives the most extensive listing of urine excretion products. Contained in this list however, are many constituents present in trace quantities only. Numerous other articles showed somewhat similar values (11)(23)(25)(26)(35).

From a review of the literature on urine, a synthetic urine was developed which had the same major chemical composition as the average values determined above. To one liter of water, the following ingredients were added in the listed quantities: urea, 20,000 mg; creatinine, 1,000 mg; sodium chloride, 8,000 mg; potassium sulfate, 1,500 mg; potassium phosphate (ortho), 1,500 mg; and ammonium chloride, 1,500 mg. The resulting composition of the synthetic is shown in Table 3.

TABLE 3
CHEMICAL COMPOSITION OF SYNTHETIC URINE
USED IN LABORATORY STUDY

Constituent	Concentration mg/l
Urea	20,000
Creatinine	1,000
Chlorides	5,845
Sodium	3,150
Potassium	1,500
Sulfates	830
Phosphates	670
Ammonium	505

The synthetic was clear to the eye, since no color or solids were added, and it had a musty odor. Chemically, however, the synthetic had the same concentrations for the major constituents as the average value for human urine.

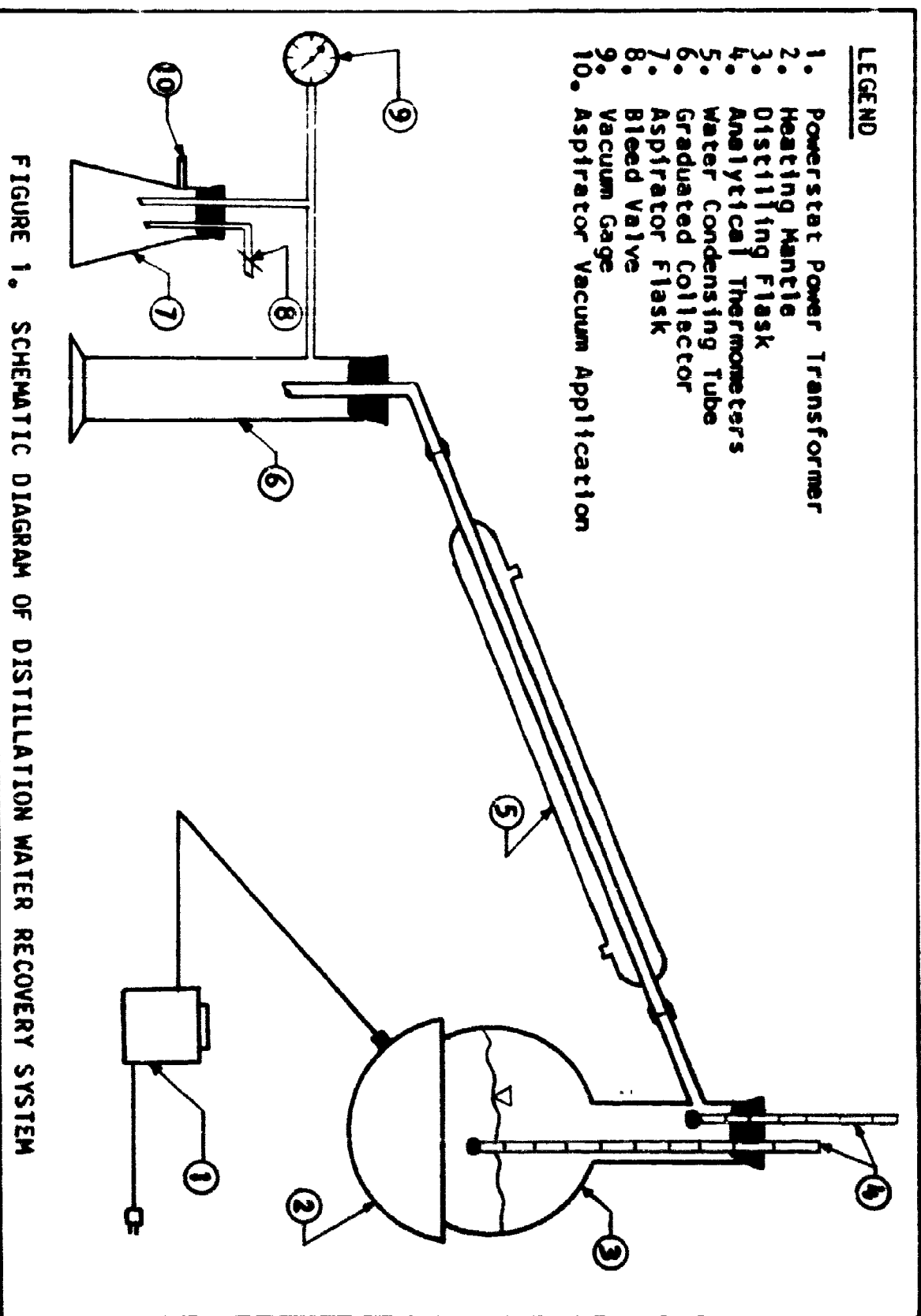
5.2 DISTILLATION OF SYNTHETIC AND HUMAN URINE

The atmospheric and vacuum distillation processes were carried out in the same still since the only difference between the two processes, from a physical requirement standpoint, is that the vacuum still must be able to withstand large differentials in pressure without leaking. Thus a vacuum still when operated at atmospheric pressures above the urine is the same as an atmospheric still.

The still used in both the distillation processes, was fabricated from existing laboratory equipment. Figure 1 shows a schematic of the distillation apparatus used in this study. Heat was supplied to the system by a Glass-Col heating mantle, Fisher catalog number 11-471V4, with the voltage to the mantle being regulated for temperature control by a Powerstat variable transformer, Fisher catalog number 9-521V2. A two liter laboratory distilling flask contained the liquid urine during the distillation processes. The top of the distilling flask was closed off with a stopper which contained two standard analytical laboratory thermometers; one providing the temperature of the liquid being distilled while the second providing the

temperature of the vapor going to the condenser. With the top of the flask being closed off, the vapor being evolved flowed into the side exit tube to which was connected a 400 mm long Graham water cooled condenser, model number 7-725. The condensed distillate flowed by gravity from the condenser to a 250 ml graduated cylinder which had a specially ground top for complete stopperage and a small exit stem placed on the side of the cylinder. This exit stem, through which the vacuum was pulled, connected to a vacuum gage to give a reading of the vacuum in the system at any time. On this same common line, there also was a standard laboratory aspirator bottle with a connection to a aspirator pump which was operated off a high capacity water line faucet. The aspirator bottle had a bleed valve to vary the vacuum to the system since the airejector pump was operated at full flow at all times.

During intial shakedown runs of the still, several problems were encountered. A large volume of foam was produced during the still's first operation with human urine. The foam was controlled by the placement of a thin layer of silicon de-foaming spray on the narrow neck portion of the distillation flask. The foam would then break as it touched the narrow walls of the flask. Another problem which occurred was that the rubber stoppers and rubber seals between glass joints gave a rubber odor to the distillate. This problem was solved by coating all rubber surfaces with



LEGEND

- 1. Powerstat Power Transformer
- 2. Heating Mantle
- 3. Distilling Flask
- 4. Analytical Thermometers
- 5. Water Condensing Tube
- 6. Graduated Collector
- 7. Aspirator Flask
- 8. Bleed Valve
- 9. Vacuum Gage
- 10. Aspirator Vacuum Application

FIGURE 1. SCHEMATIC DIAGRAM OF DISTILLATION WATER RECOVERY SYSTEM

a vacuum lubricant, Cello-Seal, Fisher catalog number 14-636. This same vacuum lubricant was also used as an extra seal on all connections to maintain pressure differentials. None of the above corrections yielded any measurable adverse effects to the system.

5.2.1 Operation of the Atmospheric Distillation System

When the still, shown in Figure 1, was used as a atmospheric distillation recovery system, no vacuum was applied to the system and the bleed valve was opened to insure that the pressure in the system was the same as the outside atmosphere. The Powerstat transformer was then turned to a setting of 120. The temperature of the urine would then gradually increase until boiling started. The vapor which was evolved was brought to the liquid state in the condenser and the distillate would flow by gravity to the graduated cylinder.

5.2.2 Operation of the Vacuum Distillation System

When the still, shown in Figure 1, was used as a vacuum distillation recovery system, a vacuum was applied to the system by a water aspirator through the aspirator stem. The bleed valve was closed and all joints and connections were coated with vacuum sealant. The vacuum was allowed to reach its maximum value of 1.5 inches of mercury above the urine samples, which usually took four minutes. The Powerstat transformer was set at 30 until the thermometer, which measured the temperature of the urine, gave

a reading of approximately 33°C . The Powerstat setting was then gradually increased until boiling started at approximately 36°C . The system had to be constantly monitored to ensure that the temperature of the urine didnot increase above 37°C , the temperature where urea begins to breakdown. The Powerstat transformer proved to be a slow method of increasing or decreasing the temperature of the urine in the flask. The remainder of the process was the same as the atmospheric distillation procedure outline in the previous section of this study.

The volume of the graduated cyclinder which collected the distillate was not large enough to hold all the distillate from a run. When the graduate would collect approximately 220 ml of distillate, the vacuum and heat were removed from the system and the distillate was poured into a nearby container. The startup process for the application of vacuum and heat was then repeated and the recovery process continued.

5.3 CHEMICAL OXIDATION OF SYNTHETIC AND HUMAN URINE

The ozonation setup used in this study was fashioned after that used by Buesher (36). Figure 2 shows a schematic arrangement with modifications of the ozonation process for the chemical oxidation of urine samples. The ozone was produced by a Welbach T-23 ozonator which used dry oxygen as the source material for ozone. The oxygen was supplied by a 500 pound gas cylinder with the

appropriate pressure reduction to approximately 10 psi. Cooling water was supplied to the ozonator from a nearby tap water faucet at a flow of 10 gallons per hour. The ozone production line was interconnected with a series of by-pass lines and valves which served the purpose of allowing the same configuration to be used for warm-up, calibration, and treatment of samples by merely opening and closing a set of valves. The settings of these valves is covered under the appropriate section for operation and calibration. The gas washing bottle, Fisher catalog number 3-040, where the ozone reacted with the sample, had a capacity of 500 ml and diffused the ozone through the sample for better contact between sample and ozone. This ozone-urine contact was also aided by a laboratory magnetic stirrer which ran throughout the process. Following the reaction flask, the unused ozone was removed quantitatively by bubbling the gas through a 2% potassium iodide solution. This ozone trap was a 500 ml Erlenmeyer flask fitted with a rubber stopper top containing two glass tubes; one bubbled the gas below the KI surface, while the other allowed the reacted gas to leave the trap. The gas then flowed through a Wet Test flow meter, Fisher catalog number 11-166-5, which gave the total gas flow for an increment of time.

LEGEND

1. Welsbach T-23 Ozonator
2. Cooling Water Lines
3. Dry Oxygen Feed Lines
4. Ozone Production Line
5. Valve
6. Gas Washing Bottle
7. Magnetic Stirrer
8. Valve
9. 3-Way Stopcock
10. Ozone Trap
11. Wet Test Flow Meter
12. Bypass Line
13. Bypass Line

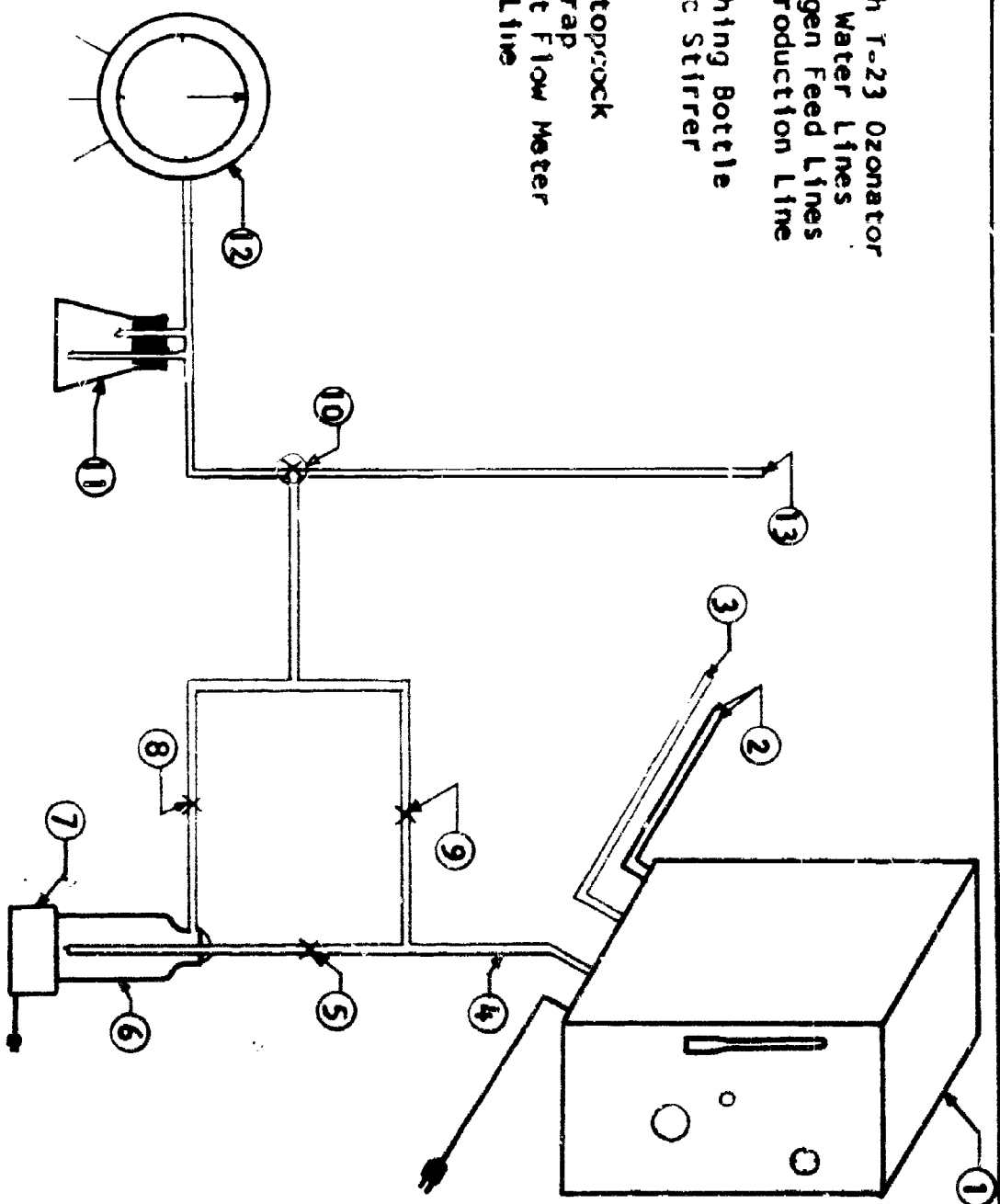


FIGURE 2. SCHEMATIC DIAGRAM OF OZONATION APPARATUS

5.3.1 Calibration of Ozonator

In order to study the chemical oxidation of urine quantitatively, the rate of ozone production must be known and be a constant value. To maintain a constant rate of ozone production with the Welsbach T-23 Ozonator, the parameters of the ozonator were always set at the same values, namely; oxygen flow was maintained at 0.01 cfm, oxygen pressure at 9.0 psig, and the voltage regulator set at 90 volts. Valves number 5 and 8, as shown on Figure 2, were then closed, valve number 9 opened, and the three-way stopcock turned so that flow was to the by-pass line (number 13). This by-pass line discharged unused ozone to the outside atmosphere where it was dispersed harmlessly. With the above settings, the ozonator was turned on. The ozonator would take 5 to 10 minutes to warm up. During this time period, 400 ml of a 2 % KI solution was placed in the ozone trap and the Wet Test meter was set at zero. A stop watch was activated at the same instant the three-way stopcock was rotated so that the ozone would flow through the ozone trap and Wet Test meter. After exactly 5.0 minutes, the three-way stopcock was again rotated so that all the flow was through the by-pass line.

The ozone production rate was calculated for the known constant ozonation settings by knowing the time and total ozone produced. The latter was calculated from the ozone's reaction with the iodide solution which liberates

free iodine. This solution was acidified and titrated with 0.1 N sodium thiosulfate solution, using starch as the endpoint indicator(37). This experimental procedure is covered more extensively in Section 6 of this thesis. Five to six calibrations were taken before and after each ozonation and the average used as the rate during the run since there was very little variation in the rate of production with the oxygen feed. Normal ozone production rates at a flow of 0.01 cfm, a pressure of 9.0 psig, and a voltage of 90 volts, with oxygen feed, varied between 27 to 28 mg/min.

5.3.2 Ozonation of Synthetic and Human Urine

After the calibration of the ozonator, the valves were reset so the ozone flow by-passed the trap and meter. Then 500 mls of the sample to under go treatment was placed in the gas washing bottle and the magnetic stirrer turned on. Simultaneously, with the aid of a fellow graduate student, valves number 5 and 8 were opened, valve 9 closed, the three-way stop-cock turned to allow flow through the trap and meter, and the stop watch started. At half-hour intervals, the valve settings were adjusted so that the ozone by-passed the sample and the trap and meter. The KI solution was then replaced and the total flow was recorded to check on flow rates. The valves were then reset to allow the ozone to flow through the sample and the trap and meter. Periodically, samples were removed in an

attempt to obtain a rate function of the oxidation process. The ozone content of the trap was analyzed immediately in accordance with the colormetric method in "Standard Methods" (37). The percent uptake of ozone versus the ozone applied to the sample was plotted during the course of the ozonation procedure in order to determine the point at which ozone was no longer being efficiently utilized by the sample.

5.3.3 Ozonation of Vacuum Distillates

The procedure for the ozonation of vacuum distillates was the same as that for the urine samples. The only difference was that the ozone traps were changed every ten minutes instead of every half-hour since the ozone was not utilized as fast by the distillates as it was by the urine and thus the KI solution would become exhausted in a shorter period of time.

6. VALIDITY OF ANALYTICAL PARAMETERS MEASURED

6.1 ROUTINE LABORATORY TESTS AND PROCEDURES

The major portion of the parameter measurements used in this study were performed in accordance with "Standard Methods for the Examination of Water and Wastewater" (37) to insure standardization of procedures and reproducibility of results. Measurements which were performed in strict accordance with "Standard Methods" were pH, chloride content, total solids (or residue), and threshold odor number determinations. The other parameters of this section had a specific method or a group of methods offered by "Standard Methods" or some modified application to the present study.

The ammonia nitrogen determinations were performed in accordance with method B, the distillation method, of the sewage section, Part II, of "Standard Methods".

The tristimulus color determinations were performed in accordance with method A, the spectrophotometric method, of the industrial wastes section, Part III, of "Standard Methods". The visible light range was scanned and recorded by a Bausch and Lomb Spectronic 505 Recording Spectrophotometer. More accurate values of purity were desired than could be obtained with the chromaticity diagrams in "Standard Methods" so the diagrams in Hardy's book (39) were consulted.

The iodometric method, method A, of determining ozone concentrations, as outlined in "Standard Methods", was employed to calculate the ozone absorbed by the urine samples. This method of determination is very accurate with errors of only plus or minus 1 % of the ozone in the sample being reported (36)(37).

The chemical oxygen demand (COD) test was performed in accordance with "Standard Methods". The high chloride content of the urine samples could have caused large errors in COD values due to the quantitative oxidation of the chlorides during the test (37)(38). This problem was remedied by the use of silver sulfate as a catalyst with a chloride correction being applied to the COD values obtained (37).

The 5-day biochemical oxygen demand (BOD) test was performed in three dilutions per sample, with each sample being replicated. The dilution, incubation, and final result calculations were conducted in accordance with "Standard Methods".

The measurement of the specific resistance was performed in accordance with the procedures for specific conductance, which is the reciprocal of specific resistance, in "Standard Methods". The measurements were performed on a conductivity bridge, Fisher catalog number 9-324V2, with a conductivity cell, dip type, which was calibrated with a standard potassium chloride solution, at 25° C, to give a cell constant for resistance measurements.

Turbidity measurements were made on a Hellige Turbidimeter, model 8000-T, with calibration charts to relate the readings back to the Jackson Turbidimeter Standard, on the SiO₂ scale, which is described in "Standard Methods".

6.2 SPECIAL PROCEDURES USED IN THIS STUDY

6.2.1 Organic Carbon Content Determinations

The determination of total organic carbon content, as a means of evaluating the quality of water, was performed on a Beckman Carbonaceous Analyzer, model IR-315. The analyzer was able to detect 99 % of carbon in a sample with a repeatability of plus or minus 1 % (40). The laboratory procedure for the use of this instrument was fashioned after that of Van Hall and Stenger (41).

6.2.2 Infrared Spectrophotometric Analysis

Absorption of organic compounds in the infrared region yields bands which are characteristic of linkages or bonds in the organic molecule. Thus infrared spectra can be applied to qualitative and quantitative analysis of organic compounds (42). This instrumentation technique has found recent application to the field of Sanitary Engineering with Liaw's study (43) of chemical oxidation of sewage where chloroform extractables of oxidized sewage were analyzed in liquid cells with IR.

For this study, the residues upon drying of human and synthetic urine for the various steps during and after the treatment processes were pressed into potassium bromide

pellets with a force of 20,000 psi in accordance with the techniques put forward by Roa (44). These pellets were then placed in a Beckman Infrared Analyzer, model IR-10, where the entire infrared region was scanned and absorption bands were continuously recorded. These infrared spectra were then interpreted by a review of the literature of past IR plots (42)(44)(45) and by private consultation with Mr. John Baum of the Chemistry Department, Washington University, St. Louis, Missouri (46).

7. EXPERIMENTAL RESULTS

7.1 ANALYSES OF URINE SAMPLES

The first phase of this study concerned itself with the complete analysis of the urine wastes, which were to undergo treatment for water recovery, using the parameters put forward in Section 4. The analyses of these urine wastes, which were the composite human urine sample and the synthetic urine sample, are shown in Table 4.

In order to check that the composite urine sample was a representative sample of human urine and to obtain a range of values for the parameters studied, individual human urine samples were also analyzed as stated earlier in Section 4 and 5 of this thesis. These individual analyses are tabulated with the composite human urine and synthetic urine results, for easy comparison, in Table 4.

7.2 RESULTS OF THE DISTILLATION RECOVERY PROCESS

Using the distillation apparatus described in Section 5.2 and the laboratory procedures outlined in Sections 5.2.1 and 5.2.2, water was recovered from the composite human urine and synthetic urine samples by the atmospheric and vacuum distillation processes. The results of the respective distillation process for the two wastes are shown in the following sections.

7.2.1 Results of Atmospheric Distillation of Human Urine

Water was recovered from 1000 ml of the composite human urine sample by the atmospheric distillation process.

TABLE 4
LABORATORY ANALYSES OF URINE SAMPLES

Parameter	Human Urine Composite	Synthetic Urine	Individual Samples	
			A	B
pH	5.9	8.7	7.1	6.7
Color				
dominant wavelength (mμ)	575	581	*	*
hue	yellow	yellowish-orange	*	*
% purity	44.9	1	*	*
% luminance	86.3	84.2	*	*
Turbidity (mg/l on SiO ₂ scale)	150	10	*	75
Specific Resistance @ 25° C (ohm-cm)	44	66	*	48
Chlorides (mg/l)	7,540	5,620	8,190	7,040
Total Solids (mg/l)	44,500	23,300	*	59,100
Threshold Odor Number	670	1	*	500
Ammonia Nitrogen (mg/l)	2,060	1,435	*	1,275
Organic Carbon (mg/l)	9,940	4,675	6,650	8,500
BOD (mg/l)	7,600	510	5,200	6,600
COD (mg/l)	18,330	7,920	13,540	16,800

* Parameter not measured

TABLE 4 (continued)
LABORATORY ANALYSES OF URINE SAMPLES

Parameter	Individual Samples				
	C	D	E	F	G
pH	6.0	5.9	5.8	5.7	6.1
Color					
dominant wavelength (mμ)	576	586	572	*	569
hue	yellow	yellowish orange	greenish yellow	*	greenish yellow
% purity	43.2	48.1	39.1	*	33.2
% luminance	86.1	83.1	89.2	*	88.1
Turbidity (mg/l on SiO ₂ scale)	40	35	45	50	80
Specific Resistance @ 25° C (ohm-cm)	48	42	61	60	96
Chlorides (mg/l)	5,560	4,340	4,070	3,660	3,120
Total Solids (mg/l)	71,100	72,800	56,600	54,600	23,700
Threshold Odor Number	*	800	650	580	510
Ammonia Nitrogen (mg/l)	2,810	3,490	2,755	2,480	975
Organic Carbon (mg/l)	12,100	13,900	13,400	12,300	5,500
BOD (mg/l)	9,900	10,700	10,200	9,060	4,420
COD (mg/l)	21,900	24,500	23,600	21,700	11,230

* Parameter not measured

TABLE 4 (continued)
LABORATORY ANALYSES OF URINE SAMPLES

Parameter	Individual Samples				
	H	I	J	K	L
pH	5.6	5.7	5.6	5.9	6.0
Color					
dominant wavelength (m μ)	576	*	581	577	*
hue	yellow	*	yellowish orange	yellow	*
% purity	45.0	*	43.3	45.9	*
% luminance	83.1	*	85.2	82.9	*
Turbidity (mg/l on SiO ₂ scale)	30	10	50	25	35
Specific Resistance @ 25° C (ohm-cm)	56	51	55	47	69
Chlorides (mg/l)	3,870	5,440	4,140	6,450	4,170
Total Solids (mg/l)	48,100	57,700	54,300	55,400	53,100
Threshold Odor Number	800	*	520	800	*
Ammonia Nitrogen (mg/l)	3,190	3,080	2,920	2,850	1,120
Organic Carbon (mg/l)	12,000	12,500	13,000	10,500	6,615
BOD (mg/l)	9,990	10,270	10,800	8,040	5,600
COD (mg/l)	21,500	21,950	23,050	18,750	12,010

* Parameter not measured

The distillation temperature was 102° C and the rate at which water was recovered was approximately 300 ml/hr. The recovery efficiency of the system was 81.2 %. The end of efficient recovery was noted by a large decrease in the specific resistance of the recovered distillate signifying a large carry-over. A sample of the distillate was removed during the earlier phases of the process to see if differences in water quality existed between initial and final recovered products. The results of this process, along with the starting composite human waste for comparison, are shown in Table 5.

7.2.2 Results of Atmospheric Distillation of Synthetic Urine

The atmospheric distillation recovery process was performed on 500 ml of the synthetic urine sample. The distillation temperature was 100° C and the rate at which water was recovered was approximately 290 ml/hr. The recovery efficiency of the system was 88.0 %. The results of this process, along with the starting synthetic urine waste, are shown in Table 6.

7.2.3 Results of Vacuum Distillation of Human Urine

Water was recovered from 1500 ml of the composite human urine sample by the vacuum distillation process. The pressure above the sample was reduced to 1.5 inches of mercury which resulted in boiling at 36° C. The recovery rate of water was approximately 60 ml/hr and the

TABLE 5
RESULTS OF ATMOSPHERIC DISTILLATION OF HUMAN URINE

Parameter	Human Urine Composite	Initial Volume of 1000 ml	
		After 250 ml Distilled	After 812 ml Distilled
pH	5.9	8.0	7.8
Color			
dominant wavelength (mμ)	575	*	578
hue	yellow	*	yellow
% purity	44.9	*	3
% luminance	86.3	*	90.5
Turbidity (mg/l on SiO ₂ scale)	150	*	10
Specific Re- sistance @ 25° C (ohm-cm)	44	775	699
Chlorides (mg/l)	7,540	41.3	47.5
Total Solids (mg/l)	44,500	*	70
Threshold Odor Number	670	*	100
Ammonia Nitro- gen (mg/l)	2,060	316	505
Organic Carbon (mg/l)	9,940	210	260
BOD (mg/l)	7,600	155	192
COD (mg/l)	18,330	479	620

* Parameter not measured

TABLE 6

RESULTS OF ATMOSPHERIC DISTILLATION OF SYNTHETIC URINE

Parameter	Synthetic Urine	440 ml of Distillate Recovered from 500 ml
pH	8.7	9.4
Color		
dominant wavelength (mμ)	581	580
hue	yellowish-orange	yellow
% purity	1	0
% luminance	84.2	98.1
Turbidity (mg/l on SiO ₂ scale)	10	5
Specific Resistance @ 25° C (ohm-cm)	66	891
Chlorides (mg/l)	5,620	39.2
Total Solids (mg/l)	23,300	102
Threshold Odor Number	1	67
Ammonia Nitrogen (mg/l)	1,435	311
Organic Carbon (mg/l)	4,675	116
BOD (mg/l)	510	98
COD (mg/l)	7,920	310

* Parameter not measured

efficiency of the water recovery system was 62.8 %. Samples of the distillate were periodically removed during the process for analysis for comparison in water quality during the recovery process. The results of this process, along with the starting composite human waste, are shown in Table 7.

7.2.4 Results of Vacuum Distillation of Synthetic Urine

The vacuum distillation recovery process was performed on 1000 ml of the synthetic urine sample. The pressure above the sample was reduced to 1.5 inches of mercury which resulted in boiling at 35^o C. The recovery rate of water was approximately 60 ml/hr and the efficiency of the water recovery system was 64.9 %. A sample of the distillate was removed at about half way through the process for comparative analysis. The results of this process, along with the starting urine waste for comparison, are shown in Table 8.

7.3 RESULTS OF THE CHEMICAL OXIDATION PROCESS

Using the ozonation apparatus described in Section 5.3 and the laboratory procedures outlined in Sections 5.3.2 and 5.3.3, the composite human urine and synthetic urine samples were ozonated in an attempt to recover potable water by chemical oxidation of the wastes. The vacuum distillates of human and synthetic urine were also ozonated in an effort to obtain a more effective treatment. The results of the ozonation process on the various samples are shown in the following sections.

TABLE 7

RESULTS OF VACUUM DISTILLATION OF HUMAN URINE

Parameter	Human Urine Composite	INITIAL URINE VOLUME OF 1500 ml		
		After 200ml Distilled	After 500 ml Distilled	After 943ml Distilled
pH	5.9	5.3	7.7	6.7
Color				
dominant wavelength (mμ)	575	*	*	578
hue	yellow	*	*	yellow
%purity	44.9	*	*	2
% Luminance	86.3	*	*	92.1
Turbidity (mg/l on SiO ₂ scale)	150	5	8	5
Specific Resistance @ 25° C (ohm-cm)	44	11,100	23,000	22,400
Chlorides (mg/l)	7,540	7.1	4.3	5.1
Total Solids (mg/l)	44,500	*	*	64
Threshold Odor Number	670	16	13	18.2
Ammonia Nitrogen (mg/l)	2,060	*	14.5	19.3
Organic Carbon (mg/l)	9,940	60	41	25.8
BOD (mg/l)	7,600	51	33.2	24.5
COD (mg/l)	18,330	141.2	96.1	51.8

* Parameter not measured

TABLE 8

RESULTS OF VACUUM DISTILLATION OF SYNTHETIC URINE

Parameter	Human Urine Composite	Initial Volume of 1000 ml	
		After 300 ml Distilled	After 649 ml Distilled
pH	8.7	8.5	8.6
Color			
dominant wavelength (m μ)	581	*	579
hue	yellowish orange	*	yellow
% purity	1	*	0.5
% luminance	84.2	*	96.3
Turbidity (mg/l on SiO ₂ scale)	10	5	5
Specific Re- sistance @ 25° C (ohm-cm)	66	22,600	38,100
Chlorides (mg/l)	5,620	4.8	3.2
Total Solids (mg/l)	23,300	*	51
Threshold Odor Number	1	*	13
Ammonia Nitro- gen (mg/l)	1,435	*	12.1
Organic Carbon (mg/l)	4,675	19	21.3
BOD (mg/l)	510	*	18.9
COD (mg/l)	7,920	*	49.6

* Parameter not measured

7.3.1 Results of Ozonation of Human urine

The chemical oxidation treatment process was performed on 500 ml of the composite human urine by bubbling ozone through the sample at a rate of 27 mg of ozone per minute. The resulting relationship between the ozone applied and the ozone absorbed is shown in Figure 3. The ozone absorbed is defined as that amount of ozone which is utilized as the ozonized oxygen passes through the sample and is equal to the amount of ozone produced minus the amount of ozone which is measured in the KI trap.

Samples were removed at various stages during the ozonation process in an attempt to obtain rates of oxidation. Also, portions of these samples from the latter periods were aerated for one-half hour before analysis to see what effects would occur. The results of this process, along with the starting composite human waste, are shown in Table 9. The rates of reduction of the principle organic parameters, by ozone, is graphically presented in Figure 4.

7.3.2 Results of Ozonation of Synthetic Urine

A 500 ml sample of the synthetic urine was ozonated at a rate of 27.5 mg of ozone per minute. The resulting relationship between the ozone applied and the ozone utilized by the sample is given in Figure 5.

Samples were removed at various stages during the ozonation process and portions of the latter samples were aerated for the same reasons and in the same manner as was

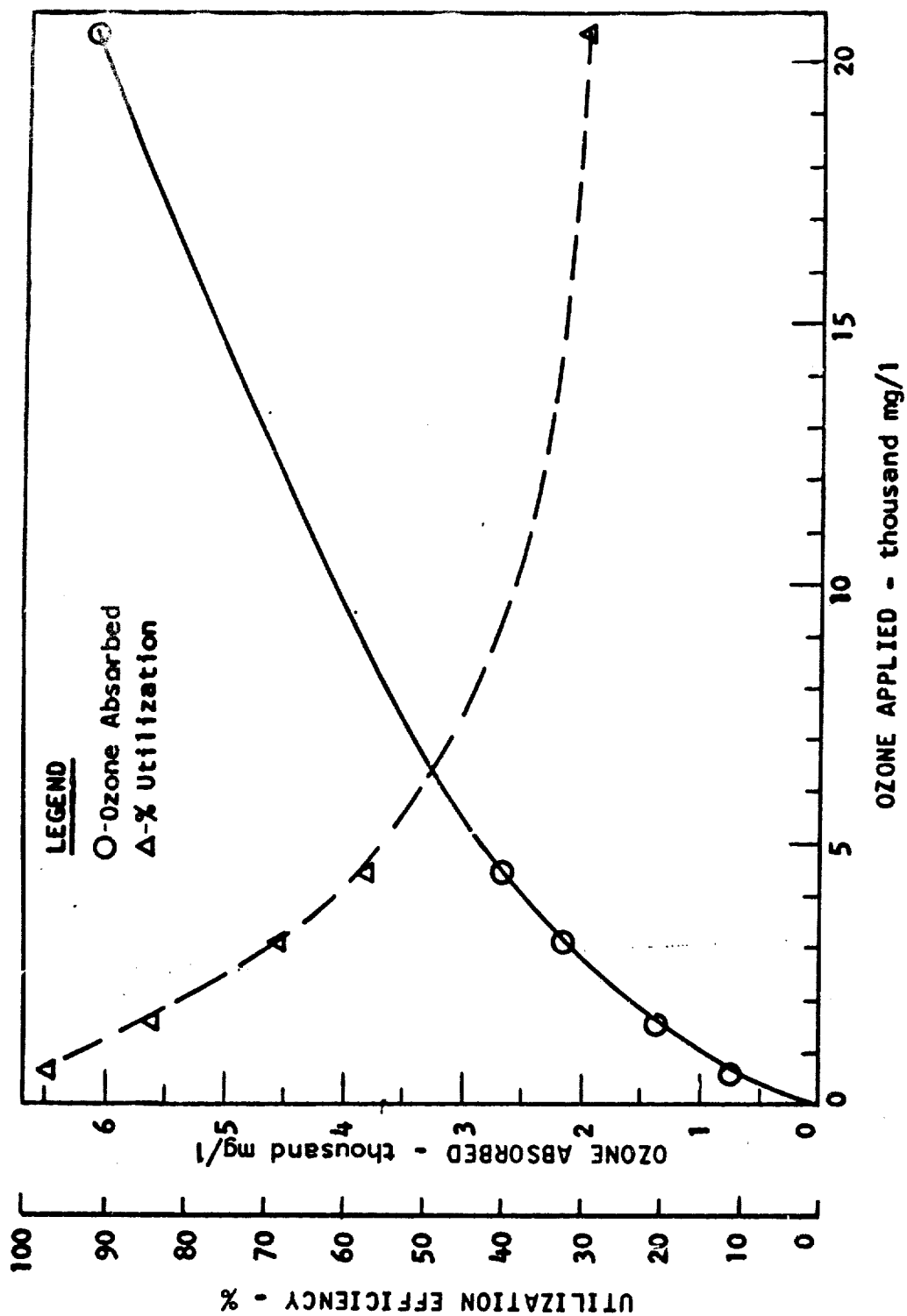


FIGURE 3. RELATIONSHIP BETWEEN OZONE APPLIED AND ABSORBED BY HUMAN URINE SAMPLE

TABLE 9
RESULTS OF OZONATION OF HUMAN URINE

Parameter	Human Urine Composite	Ozone Absorbed by Sample (mg/l)		
		786.6	1406.6	2105.6
pH	5.9	6.0	5.5	5.3
Color				
dominant wavelength (mμ)	575	*	*	*
hue	yellow	*	*	*
% purity	44.9	*	*	*
% luminance	86.3	*	*	*
Turbidity (mg/l on SiO ₂ scale)	150	26	26	70
Specific Resistance @ 25° C (ohm-cm)	1/4	44	44	43
Chlorides (mg/l)	7,540	7,400	7,450	7,400
Total Solids (mg/l)	44,500	*	*	*
Threshold Odor Number	670	1,110	1,330	*
Ammonia Nitrogen (mg/l)	2,060	1,910	2,020	1,950
Organic Carbon (mg/l)	9,940	9,490	9,480	8,700
BOD (mg/l)	7,600	*	7,420	7,050
COD (mg/l)	18,330	*	17,700	16,300

* Parameter not measured

TABLE 9 (continued)
RESULTS OF OZONATION OF HUMAN URINE

Parameter	Ozone Absorbed by Sample (mg/l)			
	2705.7	Aerated Ar- ter 2705.6	6201.2	Aerate Ar- ter 6201.2
pH	5.2	5.3	5.1	5.3
Color				
dominant wavelength (m μ)	550	552	549	*
hue	greenish yellow	greenish yellow	greenish yellow	*
% purity	26.4	26.5	20.1	*
% luminance	81.4	83.6	80.1	*
Turbidity (mg/l on SiO ₂ scale)	160	150	160	*
Specific Resistance @ 25° C (ohm-cm)	44	42	42	41
Chlorides (mg/l)	7,400	7,340	7,370	7,350
Total Solids (mg/l)	45,400	*	45,700	*
Threshold Odor Number	1,300	800	1,110	800
Ammonia Nitrogen (mg/l)	1,740	*	1,610	*
Organic Carbon (mg/l)	8,400	8,400	8,210	8,200
BOD (mg/l)	6,400	6,510	6,230	6,190
COD (mg/l)	15,750	15,430	15,010	15,130

* Parameter not measured

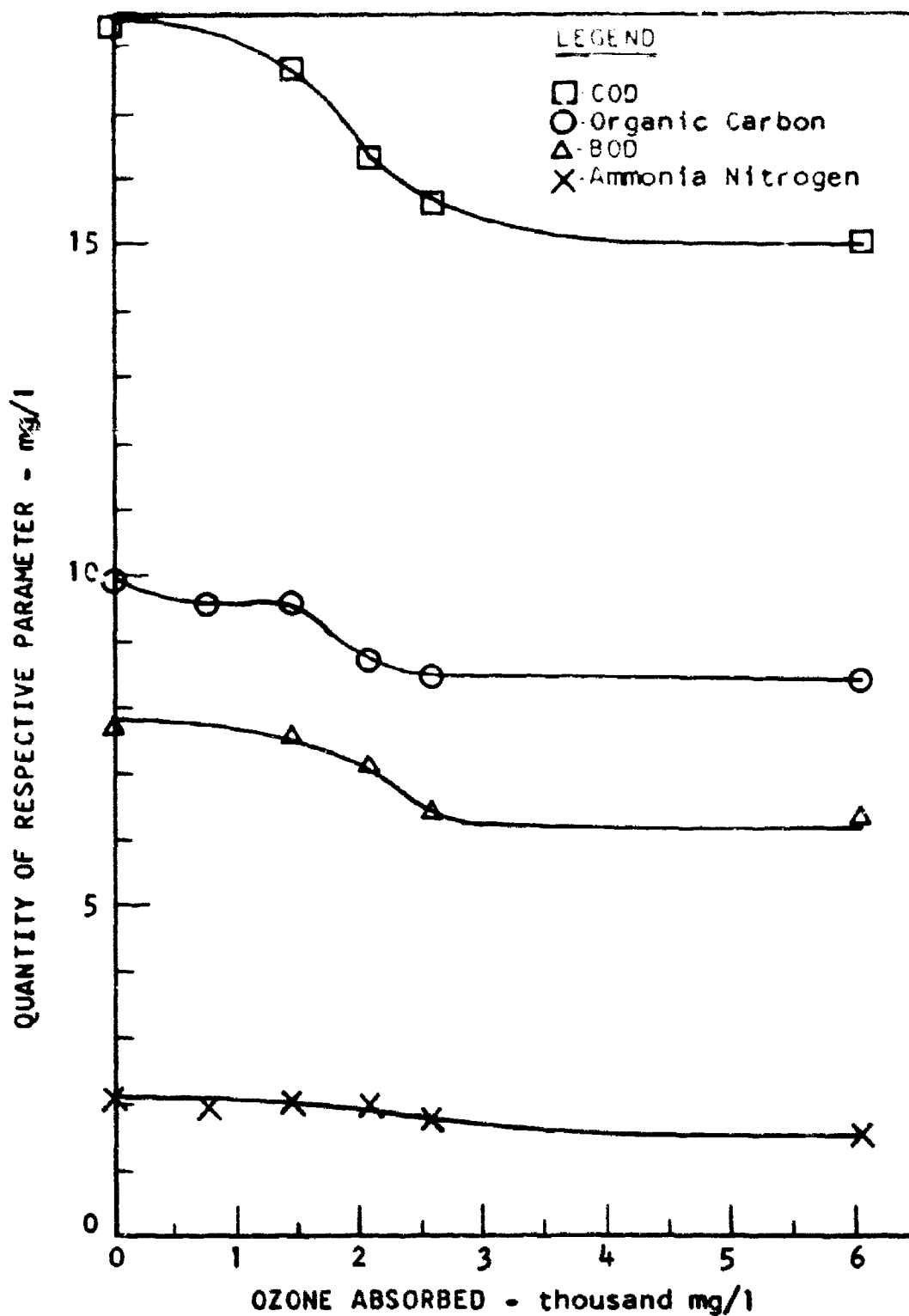


FIGURE 4. RELATIONSHIPS BETWEEN ORGANIC PARAMETERS AND OZONE ABSORBED BY HUMAN URINE SAMPLE

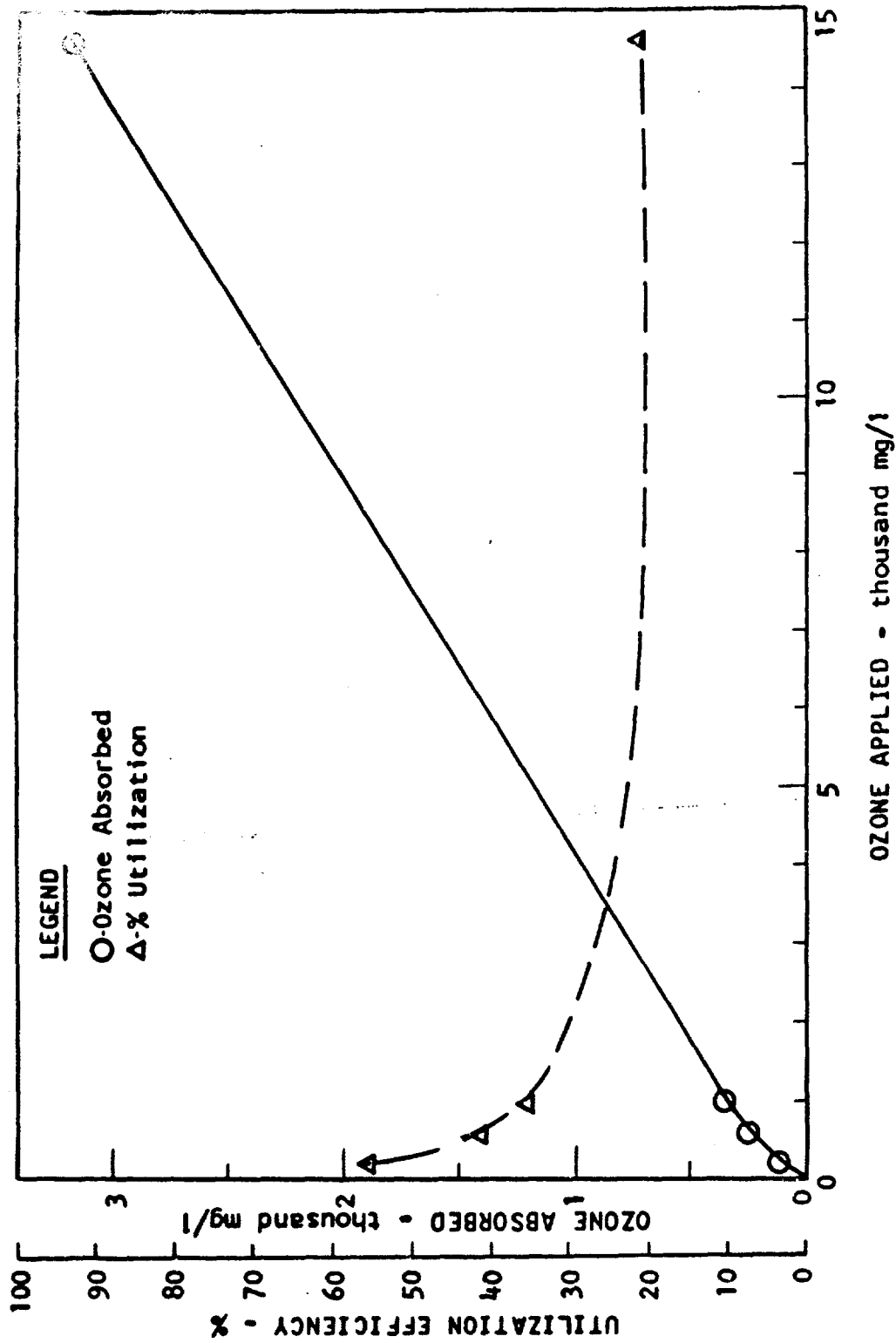


FIGURE 5. RELATIONSHIP BETWEEN OZONE APPLIED AND ABSORBED BY SYNTHETIC URINE SAMPLE

done with the human urine samples described above. The results of this process, along with the starting synthetic waste, are shown in Table 10. The rates of reduction of the principle organic parameters, by ozone, is graphically presented in Figure 6.

7.3.3 Results of Ozonation of the Vacuum Distillate of Human Urine

Due to the small volume of initial human urine used in the vacuum distillation process and the low efficiency of the recovery process, only 200 ml of the distillate was available for ozonation after the laboratory analysis. This small volume of sample did not permit a long contact time between sample and ozone due to the shallow depth of the sample in the 500 ml gas washing bottle. This fact is shown in Figure 7 by the very low efficiency of utilization between the ozone applied and the ozone absorbed by the sample. The ozone was applied at a rate of 27.5 mg of ozone per minute.

The results of the ozonation of the vacuum distillate, along with the initial starting sample (the vacuum distillate of human urine), are presented in Table 11.

7.3.4 Results of Ozonation of the Vacuum Distillates of Synthetic Urine

A small volume of the vacuum distillate of synthetic urine was available for the ozonation process for similar

TABLE 10
RESULTS OF OZONATION OF SYNTHETIC URINE

Parameter	Synthetic Urine	Ozone Absorbed by Sample(mg/l)	
		151.1	244.2
pH	8.7	8.2	8.3
Color			
dominant wavelength (mμ)	581	*	571
hue	yellowish orange	*	greenish yellow
% purity	1	*	0
% luminance	84.2	*	97.3
Turbidity (mg/l on SiO ₂ scale)	10	15	15
Specific Resistance @ 25° C (ohm-cm)	66	65	65
Chlorides (mg/l)	5,620	5,690	5,750
Total Solids (mg/l)	23,300	22,650	21,000
Threshold Odor Number	1	670	800
Ammonia Nitrogen (mg/l)	1,435	*	1,330
Organic Carbon (mg/l)	4,675	4,320	4,160
BOD (mg/l)	510	490	471
COD (mg/l)	7,920	6,910	6,280

* Parameter not measured

TABLE 10 (continued)
RESULTS OF OZONATION OF SYNTHETIC URINE

Parameter	Ozone Absorbed by Sample (mg/l)		
	Aerated After 244.2	3203.3	Aerated After 3203.3
pH	8.2	8.1	8.2
Color			
dominant wavelength (mμ)	570	570	*
hue	greenish yellow	greenish yellow	*
%purity	0	0	*
% luminance	97.6	97.5	*
Turbidity (mg/l on SiO ₂ scale)	10	20	15
Specific Resistance @ 25° C (ohm-cm)	65	64	65
Chlorides (mg/l)	5,750	5,710	5,720
Total Solids (mg/l)	20,500	20,710	*
Threshold Odor Number	500	800	670
Ammonia Nitrogen (mg/l)	1,300	1,260	*
Organic Carbon (mg/l)	3,840	3,375	3,320
BOD (mg/l)	460	416	411
COD (mg/l)	5,740	5,520	5,490

* Parameter not measured

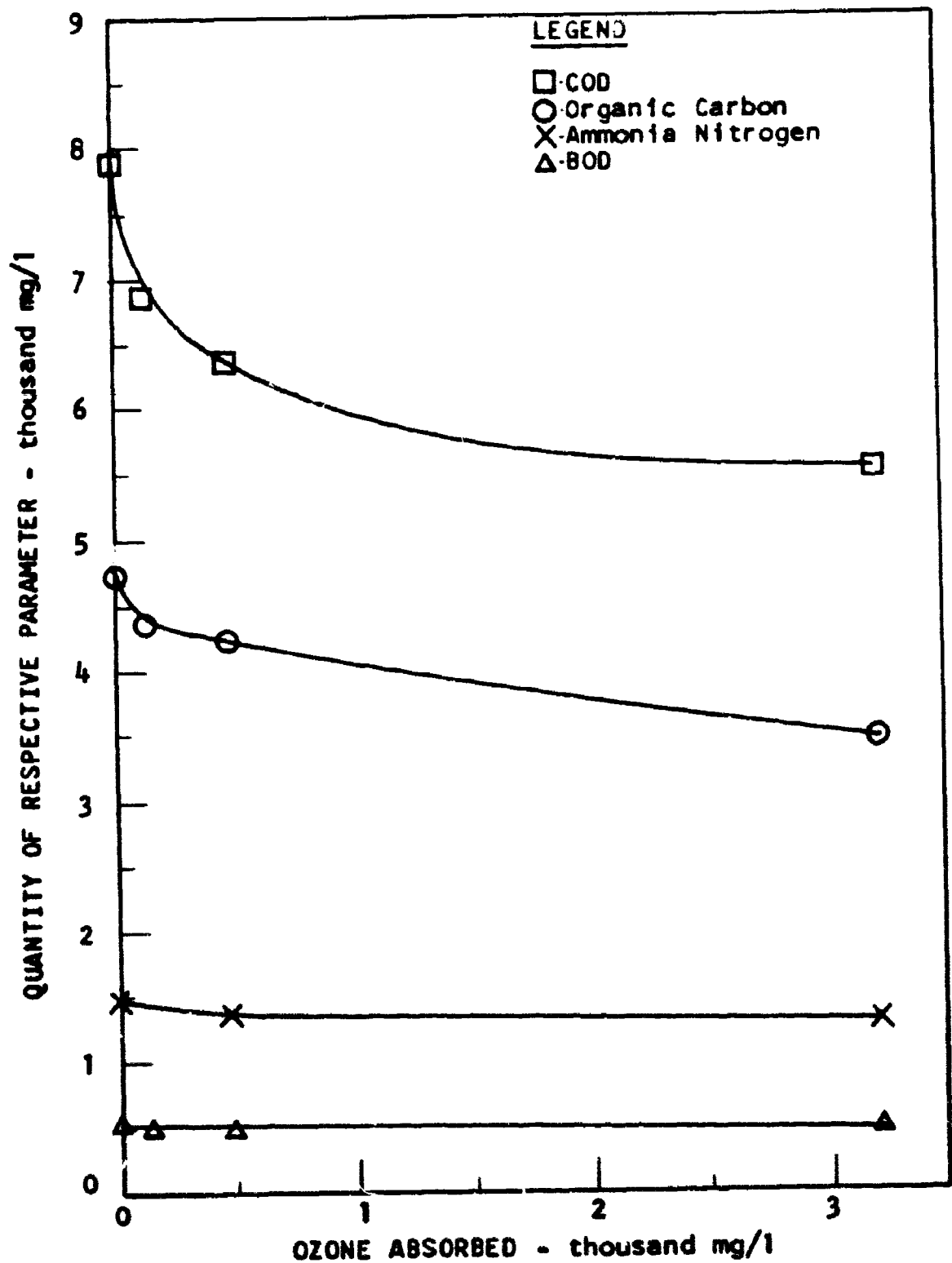


FIGURE 6. RELATIONSHIPS BETWEEN ORGANIC PARAMETERS AND OZONE ABSORBED BY SYNTHETIC URINE SAMPLE

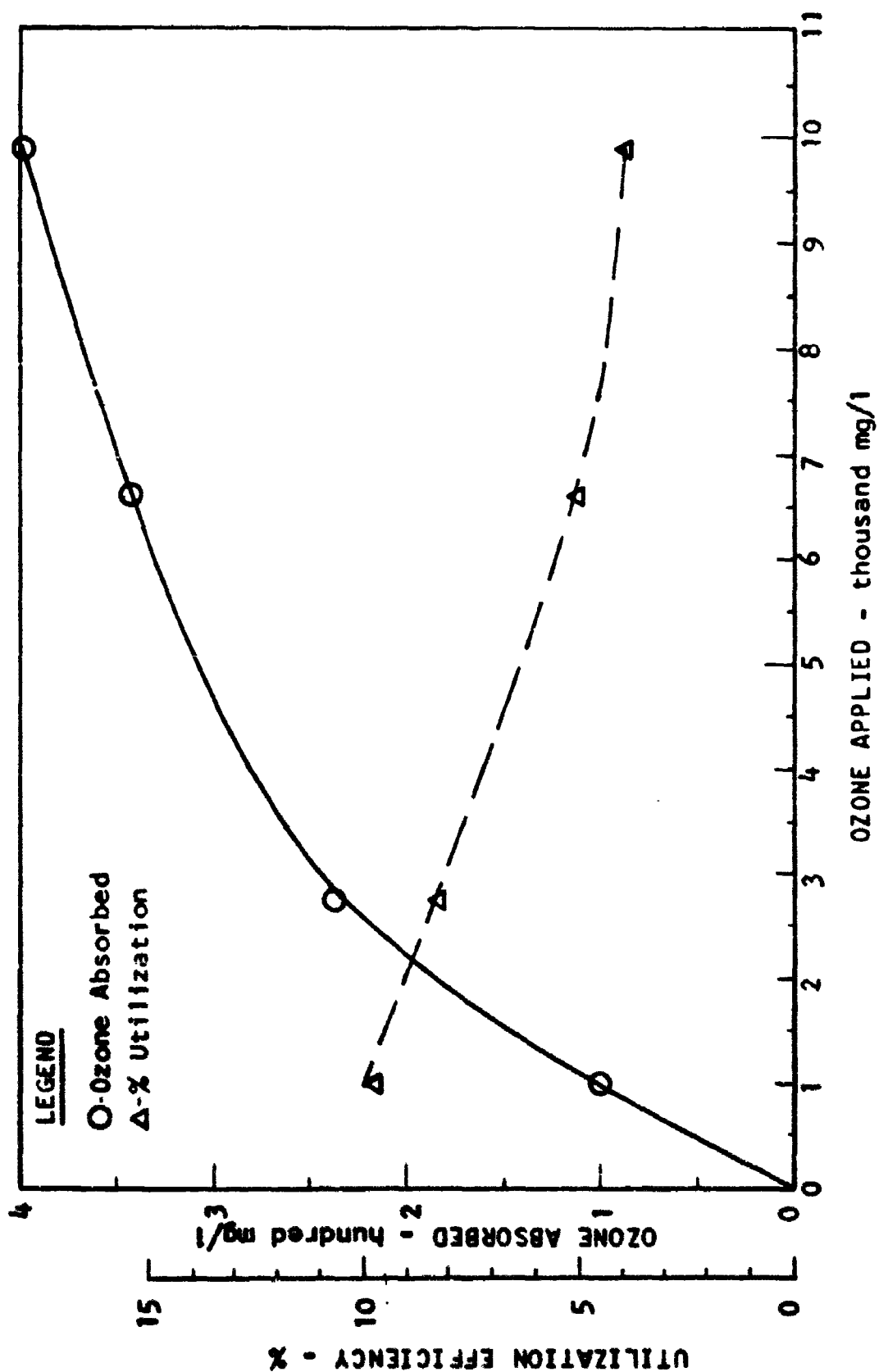


FIGURE 7. RELATIONSHIP BETWEEN OZONE APPLIED AND ABSORBED BY THE VACUUM DISTILLATE OF HUMAN URINE SAMPLE

TABLE 11

RESULTS OF OZONATION OF THE VACUUM DISTILLATE OF HUMAN URINE

Parameter	Vacuum Distillate of Human Urine	Ozone Absorbed by Sample (mg/l)	
		230.6	407.9
pH	6.7	5.3	4.8
Color			
dominant wavelength (m μ)	579	*	578
hue	yellow	*	yellow
% purity	2	*	2
% luminance	92.1	*	88.1
Turbidity (mg/l on SiO ₂ scale)	5	5	5
Specific Resistance @ 25° C (ohm-cm)	22,400	10,200	11,700
Chlorides (mg/l)	5.1	6.8	7.1
Total Solids (mg/l)	64	*	98
Threshold Odor Number	18.2	670	650
Ammonia Nitrogen (mg/l)	19.3	*	14.2
Organic Carbon (mg/l)	25.8	32.5	22.8
BOD (mg/l)	24.5	40.5	28.2
COD (mg/l)	51.8	73.1	47.5

* Parameter not measured

reasons as that of human urine. Ozone was supplied to a sample of only 175 ml of the distillate at a rate of 27.5 mg ozone per minute. The resulting relationship between the ozone applied and the ozone utilized by the sample is shown in Figure 8.

The results of the ozonation of the vacuum distillate, along with the initial starting material, are given in Table 12.

7.4 INFRARED SPECTRA OF SAMPLES

The residues of the human and synthetic urine samples collected before, during, and after the various recovery processes, were scanned in the infrared range in an attempt to qualitatively understand the water recovery processes used in this study. The procedure used was previously outlined in Section 6.2.2.

While the assignment of identities to specific compounds was not possible due to the agglomeration of substances present in the samples, it was possible to identify certain functional groupings which could then be followed through the various recovery processes.

7.4.1 Infrared Spectra of Urine Samples

The IR (infrared) spectra of the composite urine sample, from which water was recovered, is shown in Figure 9. Also presented in this figure are the spectrographs of two of the individual human urine samples, as described in Section 5.1.1, which were selected at random from the bulk of spectra of all the individual urine

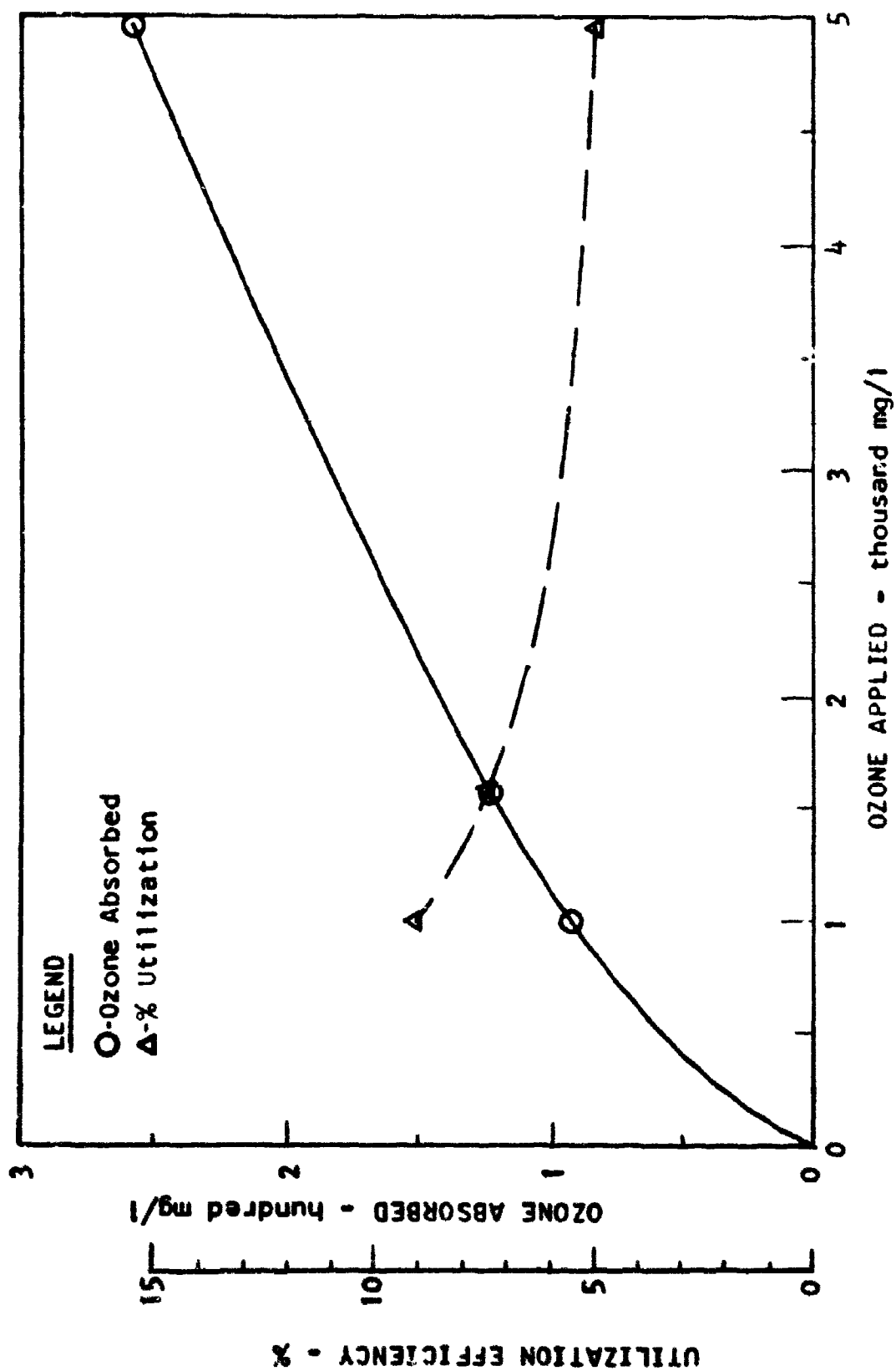


FIGURE 8. RELATIONSHIP BETWEEN OZONE APPLIED AND ABSORBED BY
THE VACUUM DISTILLATE OF SYNTHETIC URINE SAMPLE

TABLE 12

RESULTS OF OZONATION OF THE VACUUM DISTILLATE OF SYNTHETIC URINE

Parameter	Vacuum Distillate of Synthetic Urine	Ozone Absorbed by Sample(mg/l)	
		120.7	261.8
pH	8.6	7.1	6.5
Color			
dominant wavelength (mμ)	579	*	572
hue	yellow	*	greenish- yellow
% purity	0.5	*	0
% luminance	96.3	*	92.3
Turbidity (mg/l on SiO ₂ scale)	5	10	10
Specific Re- sistance @ 25° C (ohm-cm)	38,100	12,300	18,000
Chlorides (mg/l)	3.2	5.1	4.5
Total Solids (mg/l)	51	*	103
Threshold Odor Number	13	*	510
Ammonia Nitro- gen (mg/l)	12.1	*	13.2
Organic Carbon (mg/l)	21.3	20.8	20.4
BOD (mg/l)	18.9	*	18.1
COD (mg/l)	49.6	48.2	46.1

* Parameter not measured

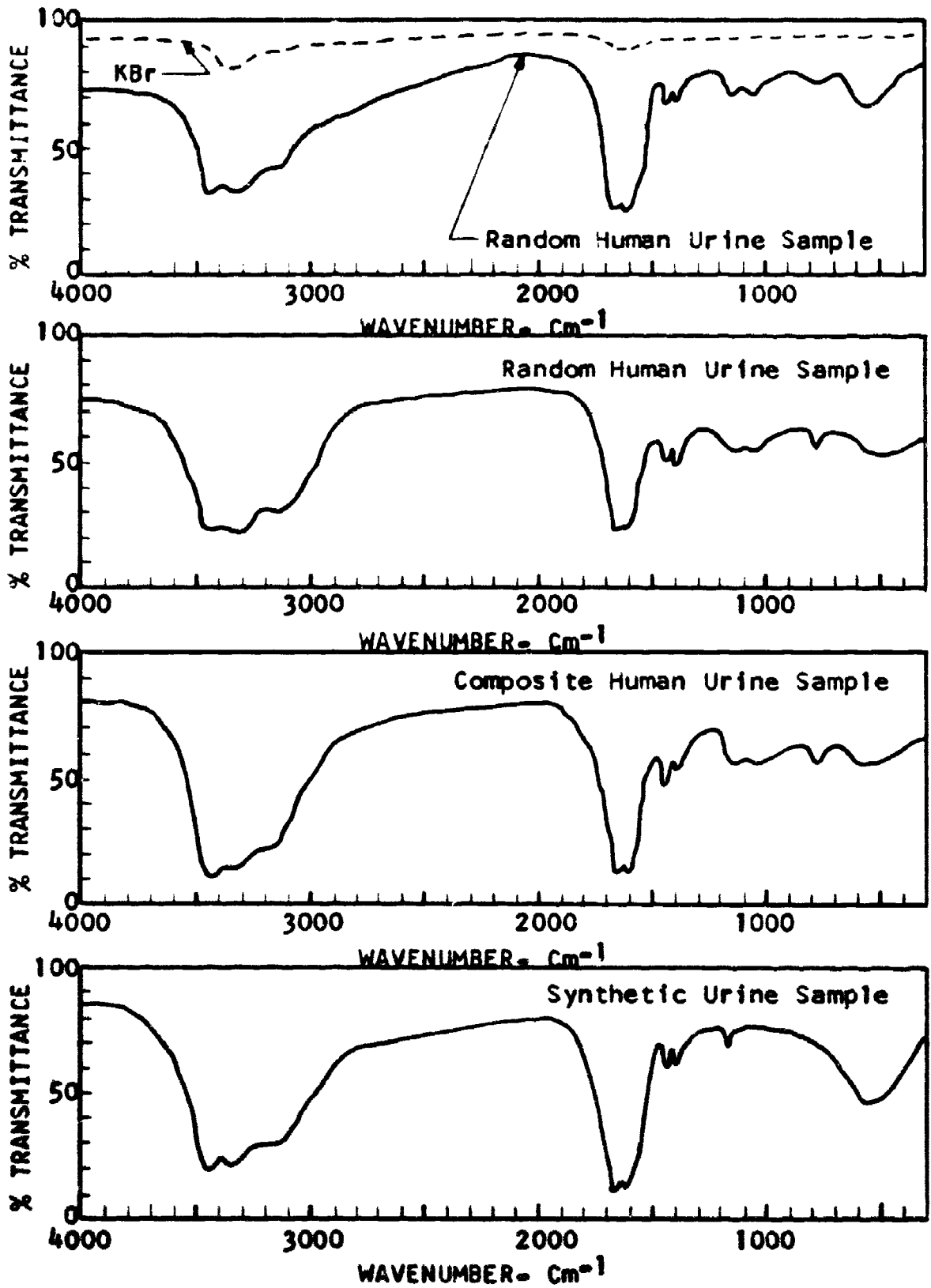


FIGURE 9. INFRARED SPECTRA OF URINE SAMPLES' RESIDUES

samples, to insure that the composite was a representative sample. The top random urine sample also has the absorption plot of potassium bromide (KBr) which formed the pellets which held all the sample residues. The synthetic urine spectrograph is also included in Figure 9 for easy visual comparison with the human urine plots.

The most predominate functional groupings of the composite human urine sample, shown on Figure 9, are the amides, $-\text{CO}-\text{NH}_2$, which have absorption bands at 3430, 3320, 1660, 1620, 1440, and 1150 cm^{-1} . The primary amine group, $-\text{CH}_2-\text{NH}_2$, have bands at 3430, 3320, 1620, 1060, and 780 cm^{-1} , parts of which overlap bands of the amide group due to the similar nature of the groups. The absorption bands at 3150 and 1400 cm^{-1} are probably those of ammonium, NH_4^+ . The broad band in the 500 to 600 cm^{-1} range could not be interpreted but may be the possible result of overtones of the amide group.

The IR spectrograph of the synthetic urine sample is also shown in Figure 9. The amide grouping is the major constituent of this spectra with absorption bands at 3420, 3310, 1660, 1610, 1440, and 1150 cm^{-1} . The ammonium bands were also present at 3160 and 1390 cm^{-1} . As was the case with the human urine sample, the synthetic spectra had a band from 500 to 600 cm^{-1} which could not be interpreted.

7.4.2 Infrared Spectra of Recovery Products of Human Urine

The infrared spectra of the atmospheric distillate of human urine, as presented in Figure 10, shows that the amide and primary amine groups, originally present in the urine, have disappeared. In their place, the following groupings were noted: A secondary amine group, $=CH-NH-CH=$, with bands at 3400, 1580, and 1100 cm^{-1} ; a alkane grouping, $-CH_3-(C=O)$, with bands at 2950, 2900, 1450, and 1400 cm^{-1} ; and a primary alcohol, $-CH_2-OH$, with bands at 3400, 1410, 1300, and 1050 cm^{-1} . Absorption bands at 780, 610, and 480 cm^{-1} also existed but they could not be interpreted using the information sources available.

The IR spectra of the vacuum distillate of human urine, as shown in Figure 10, has the same functional groups present as were interpreted in the atmospheric distillate of human urine with the exception that two of the unknown bands, one at 780 cm^{-1} and the other at 480 cm^{-1} , are not present in the vacuum distillate spectrograph.

The IR spectra of the ozonated human urine sample, as presented in Figure 10, shows the same functional groupings present as were present in the original composite urine sample. No new bands were formed or no existing bands disappeared.

The infrared spectrograph of the ozonated vacuum distillate of the human urine sample, as shown in Figure 10,

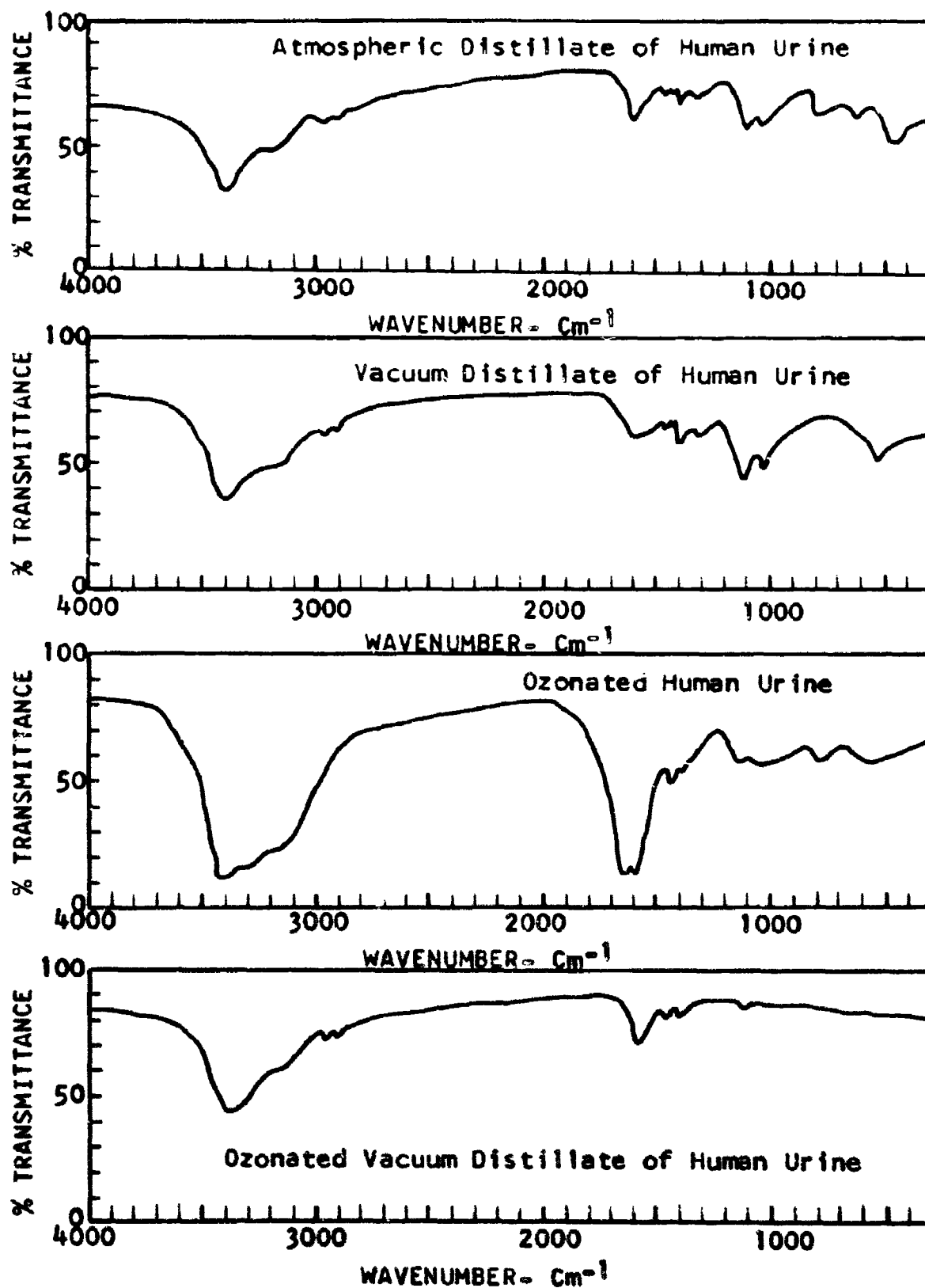


FIGURE 10. INFRARED SPECTRA OF RECOVERY PRODUCTS OF HUMAN URINE

shows that the secondary amine and the alkane grouping remained in the distillate after ozonation. The primary alcohol is not present and the ammonium absorption bands are very weak relative to the other bands.

7.4.3 Infrared Spectra of Recovery Products of Synthetic Urine

The infrared spectra of the atmospheric distillate of synthetic urine, as presented in Figure 11, shows that the amide group, which was present in the original synthetic sample, has disappeared. The ammonium ions are still present with absorption bands at 3150 and 1400 cm^{-1} . A new grouping present was a secondary amine, $=\text{CH}-\text{NH}-\text{CH}=$, with bands at 3400 , 1570 , and 1100 cm^{-1} . A carbonyl group, $=\text{C}=\text{O}$, was also suspected to be present with a band at 1710 cm^{-1} . A very strong unknown absorption band was also present at 1380 cm^{-1} and a smaller unknown band was present at 610 cm^{-1} .

The IR spectra of the vacuum distillate of synthetic urine, as shown in Figure 11, was the same as that of the atmospheric distillation of synthetic urine except that the very strong unknown absorption band at 1380 cm^{-1} was not present in the vacuum distillate.

The IR spectrograph of the ozonated synthetic urine sample, presented in Figure 11, shows the same functional

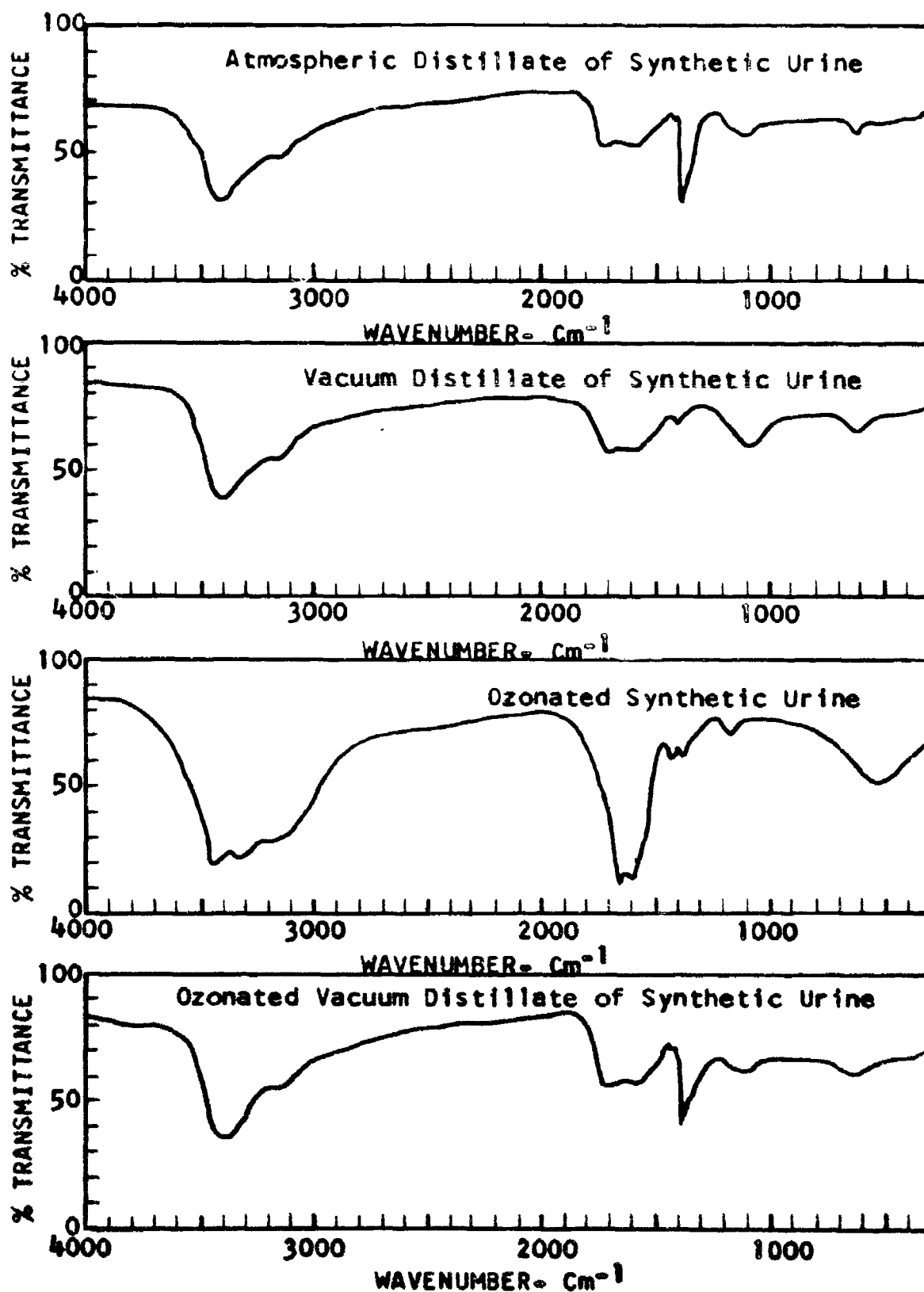


FIGURE 11. INFRARED SPECTRA OF RECOVERY PRODUCTS OF SYNTHETIC URINE

groupings present as existed in the original composite urine sample. No new bands were formed or no existing bands disappeared.

The infrared spectra of the ozonated vacuum distillate of the synthetic urine sample, as shown in Figure 11, indicates that the strong absorption band at 1380 cm^{-1} , which was present in the atmospheric distillate and not present in the vacuum distillate, has now appeared in the ozonated vacuum distillate sample. None of the other bands have changed in the sample, so that the spectra of ozonated vacuum distillate of synthetic urine is very similar to the spectra resulting from atmospheric distillation of synthetic urine.

8. DISCUSSION OF RESULTS

8.1 URINE SAMPLES

8.1.1 Human Urine Samples

The results of the analyses of the human urine samples, as earlier presented in Table 4, generally show a consistent relationship between several of the major organic parameters for the samples used in this study. These various relationships between organic carbon content and BOD values, BOD and COD values, and organic carbon content and COD values for the urine samples used in this study are shown in Figures 12, 13, and 14 respectively. From these graphic relationships, it can be observed that the composite human urine sample was truly representative of the urine samples tested. It can also be seen that, generally, ratios exist between these three organic parameters for human urine; namely, organic carbon to BOD ratio equals 1.34, BOD to COD ratio equals 0.52, and organic carbon to COD ratio equals 0.64.

The remainder of the parameters covered in Table 4 indicate that the composite sample was representative of the individual human urine samples with the exception of turbidity which was very high in the composite urine sample. The range of values for human urine as determined in Table 4 are as follows: pH ranged from 7.1 to 5.6, the color varied from yellowish-orange to greenish-yellow, the turbidity ranged from 150 to 10 mg/l on the SiO_2 scale,

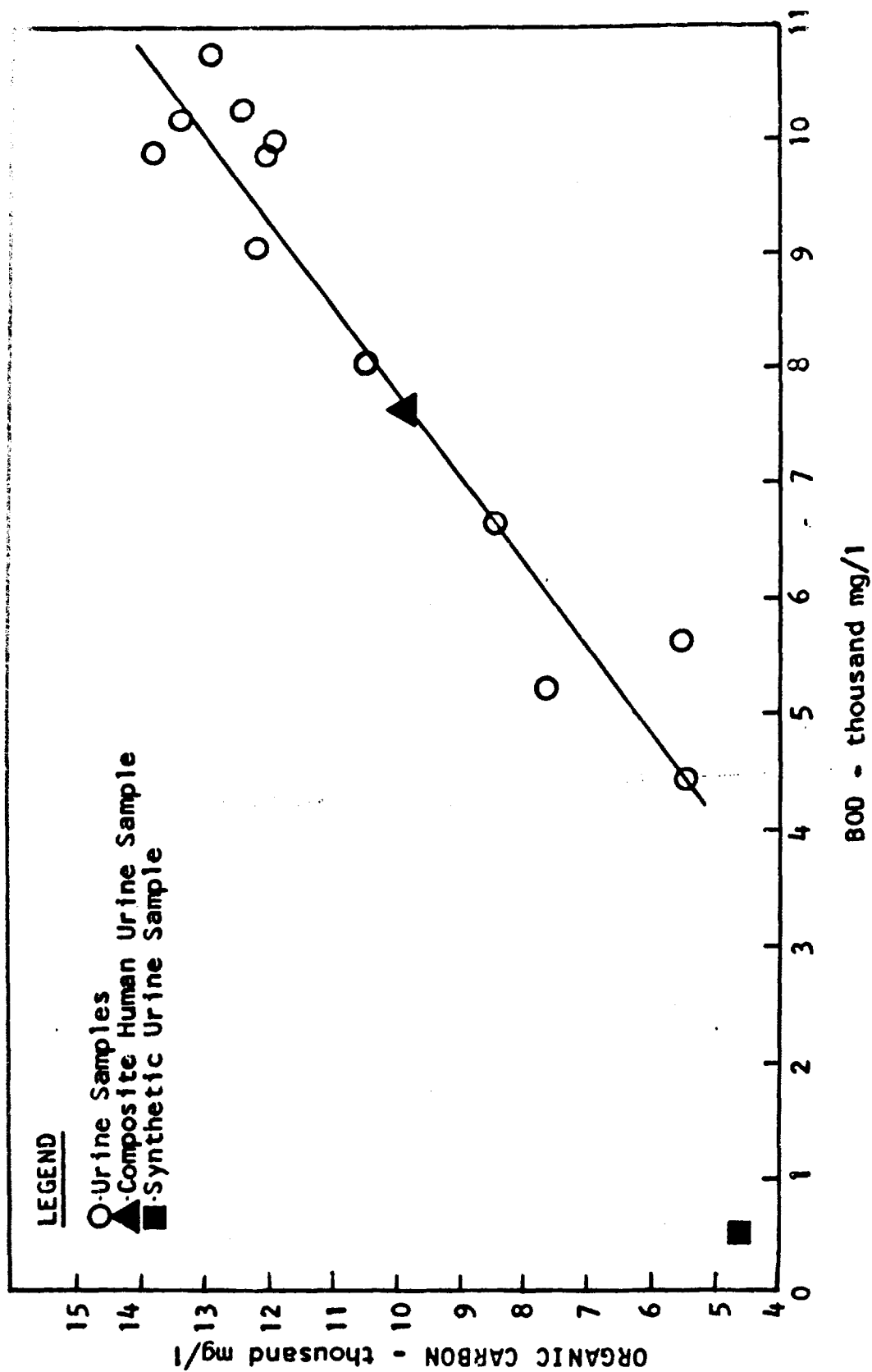


FIGURE 12. RELATIONSHIP BETWEEN ORGANIC CARBON AND BOD OF URINE SAMPLES USED IN STUDY

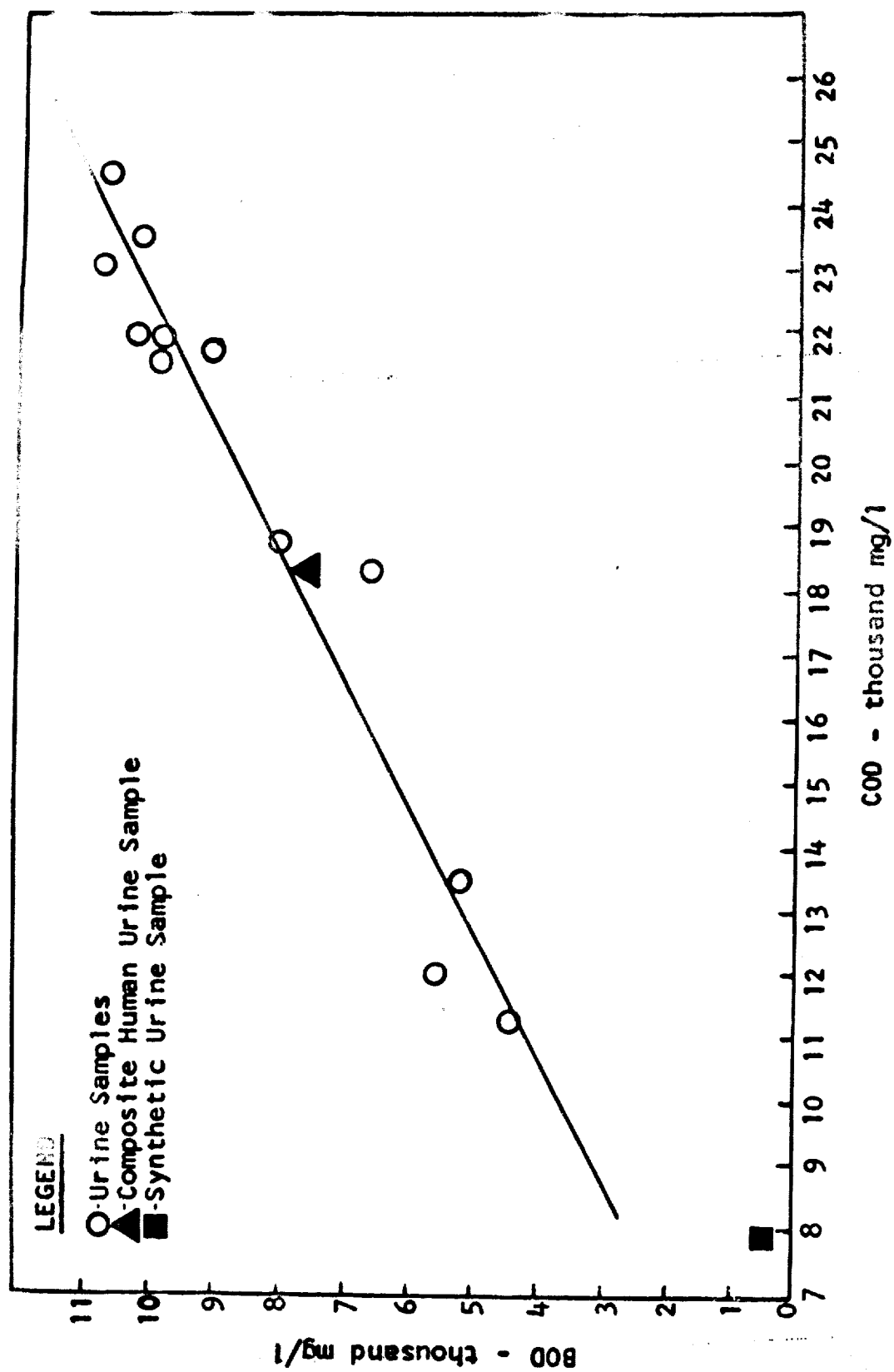


FIGURE 13. RELATIONSHIP BETWEEN BOD AND COD OF URINE SAMPLES USED IN STUDY

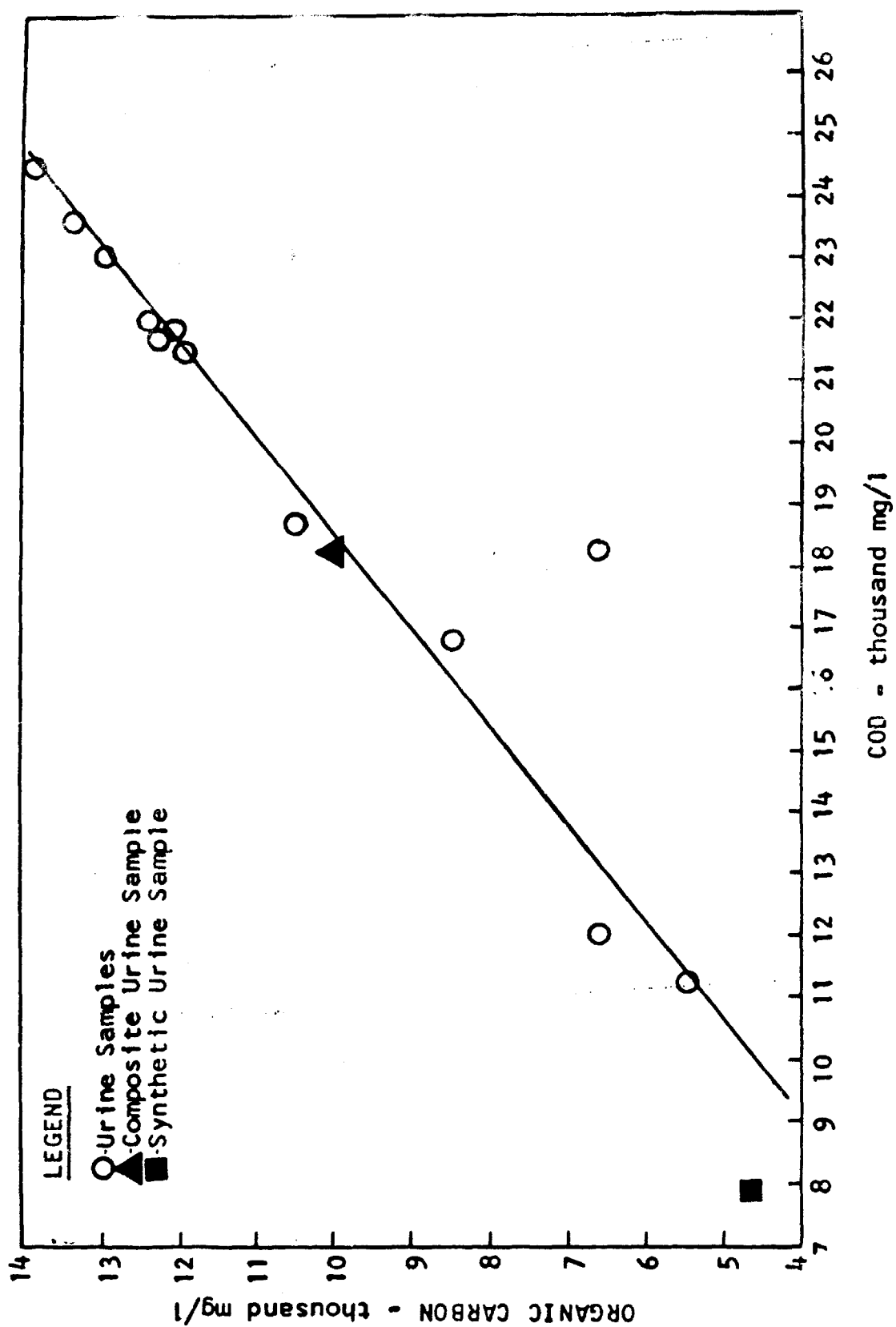


FIGURE 14. RELATIONSHIP BETWEEN ORGANIC CARBON AND COD OF URINE SAMPLES USED IN STUDY

the specific resistance at 25 °C varied from 96 to 42 ohm-cm, the chloride content ranged from 8,190 to 3,120 mg/l, the threshold odor number varied from 800 to 500, the ammonia nitrogen content varied from 3,490 to 975 mg/l, the organic carbon values ranged from 13,900 to 5,500 mg/l, the BOD ranged from 10,800 to 4,420 mg/l, and the COD varied from 24,500 to 11,230 mg/l.

The infrared studies of the residue of the composite urine sample, in Section 7.4.1, show the presence of amide, primary amine, and ammonium ion absorption bands. The predominance of these three groupings over the many functional groupings present in human urine is understandable since urea, which is a amide, accounts for approximately fifty percent of the total solids in urine(23). Also the amino acids, proteins, and other nitrogen compounds present in urine, account for a large portion of urine when they are added together as IR would do, since IR would note absorbance bands of the amine group together. The ammonium ions present are probably ammonia in equilibrium with the water in the urine. Ammonia results from the breakdown of amides and amines.

8.1.2 Synthetic Urine Sample

The analysis of the synthetic urine sample, as presented in Table 4, shows that the synthetic was low in all the parameters measured relative to the composite urine sample. The major organic parameters were plotted

along with the human urine relationship plots in Figures 12, 13, and 14 to compare the synthetic's position with the human urine range. From the results and these plots, it can be seen that the BOD is very far below the average values of the human urine samples and the other parameters are also low. Even though the synthetic's parameters had lower values than the human urine composite, the removal percentages of the major contaminants, as will be shown and discussed later, were almost identical between the synthetic and human urine samples with the exception of the BOD values. The very low BOD values of the synthetic, which is a biological measure of the organic content of a waste, was probably the result of the absence of organic contaminants which, while present in small quantities individually, add together to give human urine a high BOD value.

The infrared studies of the residue of the synthetic urine sample, in Section 7.4.1, show the presence of amide and ammonium ion absorption bands. The amide group is the result of the urea concentration of 20,000 mg/l in the synthetic. The other organic constituent, creatinine, was present at only 0.05 the concentration of urea and thus was not present in the spectra. Ammonium ions were added to the synthetic to a concentration of 505 mg/l. This value was less than that of the sulfates and phosphates and yet the ammonium absorption bands

were present in the spectra while the phosphate and sulfate were absent. This was the probable result of a breakdown of some of the urea to ammonia which went into equilibrium with the water and gave more ammonium ions.

8.2 DISTILLATION RECOVERY PROCESS

The still, which served as both the atmospheric and vacuum still as described in Section 5.2, proved to be versatile and readily adaptable to the laboratory work of this study. Considering that the still was fabricated from existing laboratory equipment, the performance was very good with the exception of the mode of temperature control. The Powerstat transformer and electric heating mantle proved to be a very slow and poor method of adjusting to or maintaining a specified temperature. Also, the distillate collector should have been as large as the capacity of the still so that the distillate would have to be removed only at the end of the process instead of interrupting the process as was the case with this study.

8.2.1 Atmospheric Distillation of Human Urine

In an attempt to correlate this study with past research in this area, the results of the atmospheric distillation of human urine are compared in Table 13 to the results of other researchers who have used the atmospheric distillation process on urine. Only two other sets of results for this process could be found in the literature. These results were from work done by Zeff(23) and

TABLE 13

COMPARISON OF RESULTS WITH PAST STUDIES USING
ATMOSPHERIC DISTILLATION OF HUMAN URINE

Parameter	This Study	Zeff (23)	Ingram (47)
pH	7.8	9.6	*
Odor	Threshold Odor No. of 100	Ammonia Odor	Strong Urinous Odor
Color	Negligible Yellow	none	*
Total Solids	70 mg/l	24 mg/l	160 mg/l
Specific Resistance @ 25° C (ohm-cm)	699 ohm-cm	660 ohm-cm	*
Chlorides	47.5 mg/l	none	*
Nitrogen	Ammonia Nitrogen of 505 mg/l	*	Total Nitrogen of 114 mg/l

* Parameter not measured

Ingram(47) and they encompassed only a portion of the parameters used in this study. The analysis of the starting wastes were not presented in these results so only the distillate quality and not the percent reduction could be compared. The data in Figure 13 seem to complement each other except that the nitrogen content of the distillate from this study is relatively high.

By comparing the atmospheric results, in Table 5, with the specifications for recovered water, in Table 2, it can be seen that the recovered water would be acceptable if not for the objectionable odor and taste.

The organic parameters dropped appreciably, as shown in Table 14, with the organic carbon decreasing by 97.4 %, the BOD decreasing by 97.5 %, and the COD decreasing by 96.7 %. These reductions still left high organic concentrations in the distillate, such as a BOD value of 192 mg/l (raw domestic sewage has a BOD of approximately 220 mg/l (37)). These high organic concentrations, which make the distillate unacceptable for human consumption without further treatment, point up the need for the inclusion of organic parameters, as well as the inorganic criteria of Table 2, in water quality standards for work in this area.

The infrared studies of the spectra of the residue of the atmospheric distillate of human urine, in Section 7.4.2, shows that the amide and primary amine

TABLE 14
PERCENT REDUCTION IN MAJOR CONTAMINANTS OF URINE
BY RECOVERY PROCESSES OF THIS STUDY

Recovery Processes		% Reduction in					
		Cl ⁻	Total Solids	Ammonia Nitrogen	Organic Carbon	BOD	COD
Atmospheric Distillation	H	99.4	99.8	75.5	97.4	97.5	96.7
	S	99.3	99.6	78.4	97.5	80.8	96.1
Vacuum Distillation	H	99.9	99.9	99.1	99.7	99.7	99.7
	S	99.9	99.8	99.1	99.5	96.3	99.4
Ozonation	H	2.5	-0.3	21.8	17.5	16.7	17.6
	S	-1.6	11.1	12.2	28.0	20.2	30.3
Vacuum Distillation Followed By Ozonation	H	99.9	99.8	99.3	99.8	99.6	99.7
	S	99.9	99.6	99.1	99.6	96.5	99.4

H = Human Urine Composite Sample

S = Synthetic Urine Sample

groups present in the human urine spectra have disappeared and the new bands of a secondary amine, alkane grouping, a primary alcohol, and three unknown bands at 780, 610, and 480 cm^{-1} are now present. The ammonium ion bands were still present. The secondary amine probably resulted from the breakdown of the primary amine in conjunction with the hydrolysis of the amide group. The appearance of an alcohol in the distillate is understandable due to its high volatility which would make the alcohol probably the first vapor to be evolved from the boiling urine. The three unknown absorption bands could not be interpreted from the information sources available. The ammonium ion absorption bands were the result of the breakdown of urea and the carry-over of ammonia gas.

8.2.2 Atmospheric Distillation of Synthetic Urine

Since the synthetic urine sample was unique to this study, a comparison with the results of other researchers was impossible. The results can, however, be compared with those of the human urine sample for the atmospheric distillation process of this study. The laboratory results, as presented in Table 6, and the comparison in percent reductions of the major contaminants, Table 14, show that the synthetic has generally the same reduction during this recovery process as the human urine sample with the exception of the BOD removal.

The distillate of the synthetic by this process was of a quality better than that required in Table 2 with the exception of the ammonia odor which was objectionable.

The infrared studies of the residue of the atmospheric distillate of synthetic urine, in Section 7.4.3, show that the amide group which was present in the original synthetic has disappeared and in its place are the absorption bands of a secondary amine, carbonyl group, a very strong unknown absorption band at 1380 cm^{-1} and a smaller unknown band at 610 cm^{-1} . The ammonium ion absorption bands were still present. The secondary amine and carbonyl groupings were the probable product of the breakdown of urea, the amide. The ammonium ion absorption bands were the result of the hydrolysis of urea and the carry-over of ammonia gas.

8.2.3 Vacuum Distillation of Human Urine

The results of the vacuum distillation of human urine, as shown in Table 7, were compared to the results of other researchers in an attempt to correlate this study with past research. This comparison with the results of research, on water recovery from urine by vacuum distillation, by Wallman (10), Ingram(11), and Zeff (23)(48) is presented in Table 15. From this table, it can be seen that the results of this study compare very favorably with past work in this area. The only discrepancy is the low pH of the distillate collected in this study.

TABLE 15
COMPARISON OF RESULTS WITH PAST STUDIES USING
VACUUM DISTILLATION OF HUMAN URINE

Parameter	This Study	Wallman (10)	Ingram (11)	Zeff (23)	Zeff (48)
pH	6.7	8.8	*	8.6	8.4
Odor	Threshold Odor No. of 18.2	Intense Odor	*	Slight Ammonia	Very Slight Ammonia
Color	Negligible Yellow	Slight	*	none	none
Total Solids	64 mg/l	38 mg/l	32 mg/l	28 mg/l	230 mg/l
Specific Resistance @ 25°C (ohm-cm)	22,400 ohm-cm	*	15,000 ohm-cm	*	*
Chlorides	5.1 mg/l	0.97 mg/l	2.1 mg/l	none	12.5 mg/l
Nitrogen	Ammonia Nitrogen of 19.3 mg/l	Free Ammonia of 28.5 mg/l	Ammonia Nitrogen of 9.0 mg/l	*	Ammonia Nitrogen of 65 mg/l

* Parameter not measured

The water recovered by vacuum distillation of human urine was of high quality far exceeding the standards of Table 2 and the slight ammonia odor would not be objectionable to a physically well trained individual for a short period of time such as a space flight (25).

The organic parameters of BOD, COD, and organic carbon all decreased by 99.7 % while the ammonia nitrogen content decreased by 99.1 % to levels more appropriate for human use (see Table 14).

The infrared studies of the residues of the vacuum distillate of human urine, in Section 7.4.2, has the same functional groupings present as were present in the atmospheric distillate of human urine with the exception of the unknown bands at 780 and 480 cm^{-1} . The groups present were secondary amines, alkanes, primary alcohol, and ammonium ions. This IR study was not quantitative but the substances present were probably at much lower concentrations than those in the atmospheric distillate due to the greater reductions in the organic parameters of the vacuum distillate over the atmospheric distillate. The absence of the absorption bands at 780 and 480 cm^{-1} show some differences do exist between the atmospheric and vacuum distillation process. It is indeed unfortunate that these absorption bands could not be identified.

8.2.4 Vacuum Distillation of Synthetic Urine

The results of the vacuum distillation of synthetic urine, as presented in Table 8, and the comparison in percent reductions, Table 14, indicate that the synthetic urine has generally the same percent reduction in the major contaminants concentration as the human urine had for this process, with the exception of the BOD removal. The distillate was of a very high quality with a minor ammonia odor.

The infrared studies of the residue of the vacuum distillate of synthetic urine, Section 7.4.3, shows that the same functional groups are present that were present in the atmospheric distillate of synthetic urine with the exception of the very strong unknown absorption band at 1380 cm^{-1} . The presence of the same grouping in the distillates of both distillation process but with the vacuum distillate not having a certain group or grouping which were present in the atmospheric distillate was common to both the human and synthetic urine samples. The groups which vanished in the cases of the two samples were different, however. These groups or groupings may be characteristic of the composition of the sample and may be affected differently by the different distillation processes.

8.3 CHEMICAL OXIDATION RECOVERY PROCESS

The ozonation apparatus, as shown in Figure 2, proved to be an effective way of oxidizing samples with ozone. The use of the dry oxygen feed, instead of the normal air feed, more than doubled the ozone production rate per unit of flow and gave more consistent production rates. One fault of the apparatus was the large number of valves that needed to be turned when the flow of ozone was changed in its direction (warm-up, calibration, by-passes, and sample treatment). This proved to be a very clumsy process always requiring two people to operate the valves if the settings were to be changed in unison.

8.3.1 Ozonation of Human Urine

The results of the ozonation of human urine, as presented in Table 9, and the comparison in percent reductions, in Table 14, indicate very low removal of the major organic parameters for high ozone dosages. The solids content apparently increased while the chloride content decreased slightly. Organically, ozone oxidizes human urine in the following quantities:

1 mg of ozone removes 0.54 mg of COD

1 mg of ozone removes 0.23 mg of BOD

1 mg of ozone removes 0.28 mg of organic carbon

1 mg of ozone removes 0.07 mg of ammonia nitrogen

The oxidizing process of ozone on the major organic constituents was presented earlier in Figure 4. From this

graph, it can be seen that the oxidation process proceeded slowly during the initial utilization of ozone by the urine. A faster rate of oxidation was observed after approximately 1600 mg/l of ozone was absorbed by the urine but the rate again tapered off after 2500 mg/l of ozone was absorbed.

The final product after the ozonation was not an acceptable water for human use. Most of the contaminants were not appreciably reduced as is shown in Table 14. In addition, the ozone appeared to combine with the urine to form a very strong nauseous odor in the product. Aerating the urine after the ozonation would reduce the odor to a degree but it had no effect on any of the other parameters.

The infrared studies of the residue of the ozonated human urine sample, in Section 7.4.2, showed the same absorption bands as were present in the initial urine sample. Since there was a reduction in the organic parameters, one of two possibilities could have occurred: First, a direct oxidation to carbon dioxide and water of the organics by the ozone without intermediate compounds being formed; or secondly, intermediate compounds were formed but were removed by the aeration effect or bubbling the ozone through the sample. The latter seems the more feasible explanation as ozone is known to oxidize unsaturated organic compounds to saturated compounds which

are then split to unsaturated compounds of lower molecular weight and then the whole cycle is repeated until CO_2 and H_2O are the final products.

8.3.2 Ozonation of Synthetic Urine

The results of the ozonation of synthetic urine, as presented in Table 10, and the comparison in percent reduction of the major contaminants in urine, in Table 14, indicate low removals for high ozone doses as was the case with the ozonated human urine sample. The major organic removals with ozone oxidizing synthetic urine were as follows:

1 mg of ozone removes 0.75 mg of COD

1 mg of ozone removes 0.03 mg of BOD

1 mg of ozone removes 0.39 mg of organic carbon

1 mg of ozone removes 0.05 mg of ammonia nitrogen

The above values differ from those of human urine with the COD and organic carbon reductions per mg of ozone greater and the BOD and ammonia nitrogen reductions per mg ozone lower than the values for human urine.

The oxidizing process of ozone on the organic constituents of the synthetic was presented earlier in Figure 6. From this graph it can be seen that the reduction rate does not proceed in the same manner as the human urine sample did. The reduction in the synthetic occurs early during the ozonation process with a very much reduced rate occurring later on. The BOD curve reflects the very small reductions in this parameter.

Generally, Table 14 shows that the synthetic urine had greater percentage reductions with less ozone application than did the human urine sample. This did not hold true for the ammonia nitrogen or BOD values.

The infrared studies of the residue of the ozonated synthetic urine sample, in Section 7.4.3, showed the same groupings present after ozonation as were present in the initial synthetic urine sample. The discussion of the ozonated human urine sample (Section 8.3.1) covers the meaning of a spectra with no change during ozonation. This discussion is applicable here.

8.3.3 Ozonation of the Vacuum Distillate of Human Urine

The results of the ozonation of the vacuum distillate of human urine, as presented in Table 11 and 14, show very little reduction in the contaminants of the distillate while showing large increases in the odor of the product. The final product was no longer useable for human consumption due to the excessive odor of the ozonated distillate.

The infrared studies of the residue of the ozonated vacuum distillate of human urine, in Section 7.4.2, indicates that the secondary amine, alkane, and ammonium ion absorption bands remained in the sample while the primary alcohol disappeared. The removal of the alcohol, which is volatile, may have been the result of the

aeration effect of bubbling the ozone through the sample rather than an oxidation process since no new bands of products formed were noted.

8.3.4 Ozonation of the Vacuum Distillate of Synthetic Urine

The results of the ozonation of the vacuum distillate of synthetic urine, as presented in Tables 12 and 14, show very little reduction in the contaminants of the distillate while showing a large increase in the odor of the product. As was the case with the human urine distillate, the ozonated distillate of the synthetic urine was no longer acceptable for human consumption due to its excessive odor.

The infrared studies of the residue of the ozonated vacuum distillate of synthetic urine, in Section 7.4.3, indicates that the strong absorption band at 1380 cm^{-1} , which was present in the atmospheric distillate and not present in the vacuum distillate, has now appeared in the ozonated vacuum distillate sample. None of the other absorption bands changed which means that the ozonated vacuum distillate and the atmospheric distillation spectra are very similar. The samples were rechecked and re-scanned by IR and the same results were obtained. This strong unknown absorption band appears, on the basis of this study, to be formed during the intense heat of boiling during the atmospheric distillation and not to be formed during the lower temperatures of vacuum distillation. It

is formed by the oxidation of the vacuum distillate with ozone while not being formed by oxidation of the synthetic urine by ozone.

8.4 DISCUSSION OF PARAMETERS USED IN THIS STUDY

As stated in Section 4.1, the parameters of pH, ammonia nitrogen, color, chlorides, turbidity, odor, specific resistance, and total solids have been used extensively by researchers in monitoring water recovery systems. They were incorporated into this study in an attempt to correlate this work with past studies. This comparison and correlation, with the above parameters, was accomplished in Tables 13 and 15. The results of this study were thus in the appropriate range of values obtained by others with water recovery from human urine.

Certain changes in the measurement of two of the above parameters, color and odor, were made in an attempt to quantitate these two parameters. In past work, color was recorded on the cobalt scale and odor was measured in terms of weak, strong, or intense. In this study, the more definite tristimulus color determinations and threshold odor number determinations were used as described in Section 6.1. The results of this study indicated that although the initial wavelength of the urine and its purity of color were valuable, the distillates were usually clear with color purities in the range of 0 to 2 %. Thus, the exact color and its concentration in the recovered

product can be measured just as effectively and much easier on the cobalt scale. Likewise with odor, the main objective is to obtain a recovery product which is not objectionable to the user. The knowledge of how bad or how good the odor is, does not concern the user as long as it is not objectionable. But for research and comparison studies, the use of a number scale for odor potential determinations of a sample is desirable.

One of the prime objectives of this study was to incorporate the parameters commonly employed by the Environmental and Sanitary Engineer, in his work in domestic water and sewage treatment, into a study of water recovery from human urine. The results of Section 7 shows that this goal was accomplished. These results also indicate that these parameters, organic carbon, BOD, and COD, are indeed effective monitors of a water recovery process from human urine as they substantiate the percent removals of the ammonia nitrogen and enhance the overall picture of the organic status of the product.

Figures 12, 13, and 14 showed that there is a general linear relationship between BOD, COD and organic carbon values for human urine. The organic carbon measurement is the easiest and fastest to measure if one has the specialized equipment. The COD and BOD tests take longer, 3 hours for COD and 5 days for BOD, but can be performed in practically every laboratory with minimal equipment.

Therefore, because linear relationships do exist for human urine between the above parameters, only one of the above tests needs to be performed after the parameters have been correlated. This one test would preferably be the organic carbon determination on a carbonaceous analyzer due to the simplicity of the determination and the almost instantaneous results.

Infrared spectroscopy of the samples before and after a respective recovery process gave a valuable insight to the functional groupings present and the resulting substances in the recovered product. Difficulty was encountered in this study in identifying certain groupings which could have greatly increased the understanding of what actually occurs during the recovery processes studied.

9. CONCLUSIONS

Based on the results obtained from the studies of water reclamation from urine by atmospheric and vacuum distillation and by chemical oxidation, the following conclusions may be drawn:

1. The organic carbon parameter is a very good monitor of a water reclamation process from urine.
2. Linear relationships exist between organic carbon content, BOD, and COD for human urine.
3. The atmospheric distillation of human urine yields a reclaimed water that has a high pH and a strong ammonia odor to it. Further treatment to remove the odor is needed if the water is to be used for drinking purposes.
4. The vacuum distillation of human urine yields a reclaimed water that has a slight ammonia odor to it but which could be used as drinking water without further treatment.
5. Chemical oxidation, by ozonation, of human urine is not recommended as large quantities of ozone are required to remove small quantities of organic contaminants. The inorganic constituents of urine are not affected by ozone. Ozone also combines with urine to form a very odorous product.

6. Ozonation of the vacuum distillate of human urine as a means of further treatment is not recommended as the large doses of ozone required for small organic removals yields a subsequent odor to the distillate which rules out its use as a water supply.
7. The synthetic urine developed in this study, while having smaller initial concentrations than human urine for many parameters, will yield comparable percentage reductions in the major parameters with human urine during the distillation recovery process with the exception of the BOD parameter.
8. Infrared spectrographic analysis can be utilized in the study of water reclamation systems to qualitatively differentiate between functional groupings present before and after the water recovery process.

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